THE APPLICATION OF pH and ORP PROCESS CONTROL PARAMETERS WITHIN THE AEROBIC DENITRIFICATION PROCESS

A THESIS SUBMITTED IN FULFILMENT

OF THE

DEGREE OF DOCTOR OF PHILOSOPHY IN CIVIL ENGINEERING

BY JOSEPH BERNARD HOLMAN

DEPARTMENT OF CIVIL ENGINEERING
THE UNIVERSITY OF CANTERBURY
NEW ZEALAND

AUGUST 2004

ACKNOWLEDGEMENTS

I would like to give sincere thanks to my Supervisor Dr David Wareham for his guidance and encouragement throughout my study. The advice and knowledge imparted by David is much appreciated.

Special thanks also to Dave MacPherson and Richard Newton (technical staff at the University of Canterbury) who provided so much input to the project from 2000-2004.

The financial support offered by the University of Canterbury through a research grant is gratefully acknowledged.

Thanks is given to the Foundation for Research Science and Technology whose support through a Bright Future Scholarship made this research possible.

Finally, thanks to my family who have made significant personal sacrifices in order for this research to be undertaken.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS
TABLE OF CONTENTS
LIST OF FIGURES AND TABLES
ABSTRACT

Chapter 1 LITERATURE REVIEW

1.1 NITROGEN IN WASTEWATER 1
1.2 NITRIFICATION 2
1.3 DENITRIFICATION 4
1.4 AEROBIC DENITRIFICATION 6
1.4.1 BIOLOGICAL EXPLANATIONS FOR AEROBIC DENITRIFICATION 8
1.4.2 PHYSICAL EXPLANATION FOR AEROBIC DENITRIFICATION 14
1.5 OPERATION OF PROBES 18
1.5.1 OXIDATION REDUCTION POTENTIAL (ORP) 19
1.5.2 HYDROGEN ION CONCENTRATION (pH) 20
1.5.3 DISSOLVED OXYGEN CONCENTRATION [DO] 22
1.6 ONLINE REAL TIME PROFILES (ORT PROFILES) 23
1.7 APPLICATION OF ONLINE PARAMETERS 28
1.8 PROJECT NEED, OBJECTIVES, AND METHODOLOGY 32
1.8.1 PROJECT NEED 32
1.8.2 PROJECT OBJECTIVES 33
1.8.3 PROJECT METHODOLOGY 34

Chapter 2 EXPERIMENTAL HARDWARE AND OPERATION

2.1 REACTORS 36
2.2 AIR SUPPLY SYSTEM 38
2.3 PROCESS CONTROL SYSTEM 41
2.4 FEED SUPPLY SYSTEM 44
2.5 EXPERIMENTAL OPERATION 46
2.6 REACTOR SEED 47
2.7 REACTOR FEED 47
2.8 REACTOR OPERATION AND CONTROL PARAMETERS 50
2.9 REACTOR COMISSIONING 52

Chapter 3 EXPERIMENTAL TESTING

3.1 TESTING UNDERTAKEN 53
3.2 SAMPLE PRESERVATION AND STORAGE 56
3.2.1 COD 56
3.2.2 TPN 56
3.2.3 NH_3-N 57
3.2.4 NO_3-N 57
3.2.5 NO_2-N, ORTHO P, AND TP 57
3.3 ON-LINE MONITORING 57
3.3.1 ORP 58
3.3.2 pH 58
3.3.3 DO 58

Chapter 4 EXPERIMENTAL RESULTS SUMMARY

4.1 INTRODUCTION TO EXPERIMENTAL RESULTS 59
4.2 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 4.0 mg/L 64
4.3 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 2.5 mg/L 70
4.4 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 1.0 mg/L 77
4.5 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 0.5 mg/L 83

TABLE OF CONTENTS

Chapter 5.0 DISCUSSION

5.1	(Objective 1) Confirm the presence of aerobic denitrification activity	89
5.2	(Objective 2) Elucidate some operational aspects of aerobic denitrification, in particular comment on the nitrification, denitrification, and sludge production rates.	91
	5.2.1 Nitrification rates	91
	5.2.2 Denitrification rates	93
	5.2.3 Sludge production rates	97
5.3	(Objective 3) Comment on the requirements for air relative to conventional separate stage nitrification denitrification processes.	98
5.4	(Objective 4) Identify the dissolved oxygen conditions necessary for aerobic denitrification and for its optimisation.	101
5.5	(Objective 5) Comment on the need for soluble organic carbon for the removal of nitrogen in the aerobic denitrification process.	107
5.6	(Objective 6) Confirm if the online profiles have unique features with respect to the aerobic denitrification process, in particular the ammonia elbow on the ORP profile and the ammonia valley on the pH profile. Correlate these online features with measured biochemical events such as the depletion of organic carbon or ammonia nitrogen.	113
	5.6.1 ORP	113
	5.6.2 pH	118
	5.6.3 Dissolved oxygen [DO]	119
	5.6.4 Air flow rate	120
5.7	(Objective 7) Develop and demonstrate control algorithms that use online features to control the aerobic denitrification process, (i.e. indirectly detect the biochemical events). In doing so demonstrate the reliability of pH and ORP control algorithms based upon relative rather than absolute values.	121
	5.7.1 ORP	121
	5.7.2 pH	122
	5.7.3 Disolved oxygen [DO]	122
	5.7.4 Air flow rate	123

Chapter 6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1	CONCLUSIONS	124
6.2	RECOMMENDATIONS	128

APPENDIX A1

A1	TRACK STUDY ONE TO TRACK STUDY SEVEN DOSP 4.0 mg/L	130-136
A2	TRACK STUDY ONE TO TRACK STUDY SEVEN DOSP 2.5 mg/L	137-143
A3	TRACK STUDY ONE TO TRACK STUDY SEVEN DOSP 1.0 mg/L	144-150
A4	TRACK STUDY ONE TO TRACK STUDY SEVEN DOSP 0.5 mg/L	151-157

APPENDIX B1

B1	PHOTOS OF EXPERIMENTAL HARDWARE	158-161
B2	SEQUENCING BATCH REACTOR OPERATIONAL PARAMETERS	162
B3	DETERMINATION OF AERATION SYSTEM EFFICIENCY	163
B4	PROCESS CONTROL SOFTWARE AND CONTROL ALGORITHMS	164-168

REFERENCES

REFERENCES 169-181

LIST OF FIGURES

Figure	Description	Page number
Figure 1.4-1	Schematic of possible dissolved oxygen profile within microbial floc (Adapted from Pochana and Keller 1999).	15
Figure 1.4-2	Representative view of sludge floc under a microscope with suggested zones for nitrification and denitrification. (Adapted from Demoulin *et al* (2001)).	16
Figure 1.5-1	Diagram of an ORP electrode and operation	19
Figure 1.5-2	Diagram of a pH electrode	22
Figure 1.6-1	Generalized schematic of ORP, pH, and DO profiles, main bending points illustrated.	23
Figure 1.6-2	Typical ORP vs time profile showing nitrate breakpoint (adapted from Wareham *et al* (1993))	26
Figure 1.7-1	Typical ORP profile for A/O BNR plant (adapted from NZWWA, 1997)	31
Figure 2.1-1	Diagram of one sequencing batch reactor	36
Figure 2.2-1	Aeration system for set points down to 1.0 mg/L (Duplicated for second reactor).	39
Figure 2.2-2	Aeration system for set points below 1.0 mg/L (Duplicated for second reactor)	40
Figure 2.3-1	Process control system (with attached hardware)*	43
Figure 2.4-1	Heating of wastewater	46
Figure 2.5-1	Representative configuration of the SBR process.	47
Figure 2.7-1	Schematic of Bromley wastewater treatment plant with the location of experimental feed collection indicated, (Adapted from Christchurch City Council public information brochure).	48
Figure 2.7-2	Organic carbon degradation during wastewater storage	50
Figure 4.1-1	Effect of DO concentration on SRT required to achieve effluent ammonia concentrations less than 1.0 mg/L in a completely mixed activated sludge system (adapted from Metcalf and Eddy	59
Figure 4.2-1	Mixed liquor suspended solids concentration DOSP 4.0 mg/L	64
Figure 4.2-2	Mixed liquor wastage DOSP 4.0 mg/L	65
Figure 4.2-3	Solids residence time DOSP 4.0 mg/L	65
Figure 4.2-4	pH and [soluble nitrogen]	68
Figure 4.2-5	Air flow rate [NH3-N] and [COD]	68
Figure 4.2-6	ORP and [DO]	69
Figure 4.3-1	Mixed liquor suspended solids concentration DOSP 2.5 mg/L	70
Figure 4.3-2	Mixed liquor wastage DOSP 2.5 mg/L	71
Figure 4.3-3	Solids residence time DOSP 2.5 mg/L	71
Figure 4.3-4	pH and [soluble nitrogen]	74
Figure 4.3-5	Air flow rate [NH_3-N] and [COD]	74
Figure 4.3-6	ORP and [DO]	75
Figure 4.4-1	Mixed liquor suspended solids concentration DOSP 1.0 mg/L	77

LIST OF FIGURES

Figure	Description	Page number
Figure 4.4-2	Mixed liquor wastage DOSP 1.0 mg/L	78
Figure 4.4-3	Solids residence time DOSP 1.0 mg/L	78
Figure 4.4-4	pH and [soluble nitrogen]	81
Figure 4.4-5	Air flow rate [NH3-N] and [COD]	81
Figure 4.4-6	ORP and [DO]	82
Figure 4.5-1	Mixed liquor suspended solids concentration DOSP 0.5 mg/L	83
Figure 4.5-2	Mixed liquor wastage DOSP 0.5 mg/L	84
Figure 4.5-3	Solids residence time DOSP 0.5 mg/L	84
Figure 4.5-4	pH and [soluble nitrogen]	86
Figure 4.5-5	Air flow rate, [NH_3-N] and [COD]	87
Figure 4.5-6	ORP and [DO]	88
Figure 5.2-1	Nitrification rate versus dissolved oxygen concentration	91
Figure 5.2-2	Extension in aeration time required to oxidise ammonia nitrogen (relative to DOSP 4.0 mg/L)	92
Figure 5.5-1	Cycle illustrating nitrogen removal rate versus soluble organic carbon availability	107
Figure 5.5-2	PHB (poly-B-hydroxybutyrate)	109
Figure 5.6.1-1	Illustration of ORP elbow in an A/O process. (Figure Adapted from Yu *et al* (1998)	114
Figure 5.6.1-2	Illustration of ORP elbow in an A/O process. (Figure Adapted from Ra *et al* (2000)	115
Figure 5.6.1-3	Illustration of ORP ammonia elbow in an aerobic denitrification process, Holman and Wareham (2003), (note anoxic phase for first 10 minutes). *First ORP elbow resulted from organic carbon depletion, not shown.	115
Figure 5.6.1-4	Illustration of ORP elbow in aerobic sludge digestion process. (Figure adapted from Wareham *et al* 1993).	116
Figure 5.6.1-5	Illustration of absence of ORP ammonia elbow when dissolved oxygen concentration maintained at a consistent level (taken from TS1 DOSP 4.0 mg/L).	116
Figure 5.6.2-1	Typical pH profile, (aeration starts at time = 0)	119
Figure 5.6.4-1	Typical air flow profile	120

LIST OF TABLES

Table	Description	Page number
Table 2.7-1	Influent wastewater characteristics	49
Table 2.7-2	Wastewater degradation while in cold storage	49
Table 3.1-1	Chemical parameters monitored	53
Table 3.1-2	Chemical parameters analyzed using colorimetric methods	54
Table 3.1-3	HACH nitrogen tests used in this research	55
Table 4.1-1	Summary of results DOSP 4.0 mg/L – 0.5 mg/L	63
Table 4.2-1	Summary of track study data [operational dissolved oxygen] 4.0 mg/L	66
Table 4.2-2	Summary of HRT values DOSP 4.0 mg/L	66
Table 4.3-1	Summary of track study data [operational dissolved oxygen] 2.5 mg/L	72
Table 4.3-2	Summary of HRT values DOSP 2.5 mg/L	73
Table 4.4-1	Summary of track study data [operational dissolved oxygen] 1.0 mg/L	79
Table 4.4-2	Summary of HRT values DOSP 1.0 mg/L	79
Table 4.5-1	Summary of track study data [operational dissolved oxygen] 0.5 mg/L	85
Table 4.5-2	Summary of HRT values DOSP 0.5 mg/L	85
Table 5.2-1	Aeration time relative to dissolved oxygen concentration	92
Table 5.2-2	Comparison of biochemical transformation rates between conventional and aerobic denitrification processes.	95
Table 5.2-3	Normalized sludge production	97
Table 5.3-1	Total air required for ammonia oxidation	98
Table 5.4-1	Effect of dissolved oxygen concentration on aerobic nitrogen losses	101

ABSTRACT

Aerobic denitrification is a biological nitrogen removal process in which nitrification and denitrification occur simultaneously (in the same reactor) under identical environmental conditions. This contrasts to traditional separate stage nitrification denitrification in which the nitrification and denitrification processes occur sequentially in different reactors under opposing environmental conditions. While aerobic denitrification has long been identified in other ecosystems (such as the nitrogen cycle within soil) it was not thought possible within wastewater treatment processes. The existence of aerobic denitrification within wastewater treatment systems was first identified in the early 1980's following nitrogen mass balances that suggested unexplained nitrogen losses were occurring in the aeration tanks of many full-scale biological nutrient removal facilities (total nitrogen losses of up to 30% were frequently occurring U.S.EPA (1987)). Since then researchers and engineers have attempted to elucidate the mechanics behind the aerobic denitrification phenomenon and the conditions required for its optimization. It is thought that aerobic denitrification may offer advantages and possible savings when compared to alternative traditional separate stage nitrification denitrification processes.

The use of real time parameters such as ORP, pH, DO and airflow rate (oxygen demand) can provide immediate insight into a biological treatment process. This knowledge can be used to ensure optimum performance in terms of real time pollutant concentrations and hydraulic loads. This research aimed to elucidate some operational aspects of the aerobic denitrification phenomenon, to investigate opportunities for several types of real time control (ORP, pH, DO, and airflow), and to develop a process control system using the online parameters.

An activated sludge process was established within two lab-scale sequencing batch reactors. The reactors were operated under a range of conditions using raw domestic wastewater as the feed. ORP, pH, DO, and airflow were measured

online in real time while other biochemical parameters (such as the various forms of nitrogen) were measured periodically using HACH photometric procedures. Dissolved oxygen concentration was the operational variable (dissolved oxygen set points (DOSP) 4.0–0.5 mg/L), other parameters such as MLSS concentration and feed strength were maintained (where possible) at a consistent value (~3000 mg/L and ~ 600 mg/L COD respectively). The system was operated under both nitrification and aerobic denitrification conditions with the dissolved oxygen concentration determining the degree to which aerobic denitrification existed (~40% TN removal at DOSP 0.5 mg/L).

The biochemical event of interest was the depletion of ammonia nitrogen. The key online profiles of interest were the ORP-time profile and the pH-time profile. The research sought to demonstrate the credibility of ORP and pH as real time control parameters for the depletion of ammonia nitrogen in the aerobic denitrification process. To achieve this a microprocessor-software based process control system was developed by using the relationship between online measurements and biochemical events.

The results indicated the ORP-time profile does not provide any feature for the depletion of ammonia nitrogen when the dissolved oxygen is maintained at a fixed concentration. That is the previously identified "ammonia elbow" is probably the result of dissolved oxygen concentration breakthrough rather than nutrient depletion. The lack of an ammonia depletion elbow meant that ORP could not be used for process control within the aerobic denitrification process. The pH-time profile showed an "ammonia valley" feature at the point of ammonia depletion. This feature was consistently present in both the nitrification and aerobic denitrification processes. The research incorporated the feature into the process control system and successfully used it to control the length of the aerobic denitrification treatment sequence. With respect to elucidating some operational aspects of the aerobic denitrification phenomenon the main variable of interest

was the dissolved oxygen concentration. The results indicated the aerobic denitrification process has an optimum dissolved oxygen concentration around but probably below 0.5 mg/L. The process probably does not have an optimum concentration but an optimum range. It is likely this range is influenced by variables such as the biomass concentration and the release of reducing power in terms of the ability to hydrolyze stored carbon polymers.

A secondary objective of this research was to elucidate advantages of aerobic denitrification relative to alternative traditional separate stage nitrification denitrification processes. For example it has been proposed that aerobic denitrification may require smaller treatment reactors, require less air for nitrification, produce less sludge per unit of wastewater treated (relative to a traditional nitrification-denitrification process), and have less dependence on organic carbon for denitrification.

The results suggested the low dissolved oxygen concentrations required for the aerobic denitrification process significantly inhibit the nitrification process. This causes a considerable extension in the required aeration times for the oxidation of ammonia nitrogen (~300% increase in aeration time relative to a traditional nitrification process). The longer aeration times suggest the process may not offer savings in terms of aeration requirements (aerobic denitrification required ~200% more air per unit of wastewater treated relative to a traditional nitrification process) or treatment tank sizes (relative to traditional separate stage processes).

A reduction in the quantity of sludge produced (per unit of wastewater treated) of over 30% was demonstrated for the aerobic denitrification process. While aerobic nitrogen removal has been achieved under certain conditions autotrophically by

other researchers this work found the process is probably undertaken predominantly by heterotrophic micro-organisms. The low dissolved oxygen concentrations required for the process also appear to favor heterotrophic denitrification using stored intracellular carbon (biosorption). This research demonstrated the aerobic denitrification process was able to remove nitrogen with less dependence on organic carbon (the organic carbon requirements for aerobic denitrification were not quantified but experimental data suggests a possible 40% saving) either by the use of a shortened nitrification-denitrification pathway and/or the ability to use stored carbon.

Chapter 1 LITERATURE REVIEW

1.1 NITROGEN IN WASTEWATER

Untreated wastewater typically contains nitrogen in one of five forms. These are organic nitrogen, ammonia nitrogen (NH_3-N) ammonium nitrogen (NH_4^+-N), nitrite nitrogen (NO_2-N), and nitrate nitrogen (NO_3-N). The organic and ammonia nitrogen forms predominate. Organic nitrogen is converted to ammonia nitrogen as cells die and bacterial decomposition of matter occurs. Ammonia nitrogen exists either as the ammonium ion or as ammonia depending upon the pH, at pH levels below 9 the ammonium ion predominates (Metcalf and Eddy (2001)).

Primary and secondary treatment facilities do not remove nitrogen from wastewater. Typically nitrogen remains in the organic, ammonia nitrogen, or nitrate nitrogen forms. In some instances the discharge of nitrogen in treated effluents may pose an environmental or public health risk. Nitrogen in the form of organic nitrogen, ammonia, or the ammonium ion can exert an oxygen demand on the receiving water body as it is transformed to an oxidized form. Nitrogen in the ammonia and nitrite forms is known to be toxic to fish. Nitrate is a biostimulant which may cause eutrophication of water bodies and has also been linked to methemoglobinemia or blue baby syndrome in infants when present in drinking water supplies (particularly contaminated ground water sources) (Spalding and Exner (1993), Azov *et al* (1995), Meinardi *et al* (1995), Agrawal *et al* (1999), Addiscott (2000)).

Due to the potential environmental and public health impacts the removal of nitrogen from wastewater is becoming a requirement in many developed countries. For example, countries within the European Union (EU) are increasingly specifying nitrogen removal as a treatment objective (Fuerhacker *et al* (2000)). Typical nitrogen removal rates (such as those required in Austria) include 60-70% nitrogen removal (BGBl 210/1996) with a decrease in NH_4-N and

NO_3-N to below 10 mg/L. The removal of nitrogen is also an economic necessity for some European wastewater plants. New environmental protection legislation has seen penalty taxes applied to nitrogen in wastewater effluents. For example in Denmark the discharge of nitrogen from treatment plants is now taxed at a rate of $US2.40/kg (Cecil (2003)). Cecil (2003) investigated the Ejby Molle plant in Denmark and reported possible penalty tax savings of $US 48,000 per year for every 1mg/L of N that could be removed. The removal of nitrogen is typically achieved in two separate stages, these are called nitrification and denitrification.

1.2 NITRIFICATION

Nitrification involves two steps the first being the biological oxidation of the ammonium ion, (NH_4^+) to nitrite nitrogen (NO_2^-) as shown in equation (1.2-1).

Step One – (Nitrification)

$$5NH_4^+ + 76O_2 + 109HCO_3^- \xrightarrow{Nitrosomonas} C_5H_7NO_2 + 54NO_2^- + 57H_2O + 104H_2CO_3$$

Oxidation state of nitrogen = $^-3$
$^-3 + {}^+4 = {}^+1$

Oxidation state of nitrogen = $^+3$
$^+3 + {}^-4 = {}^-1$

Equation 1.2-1 First stage of nitrification.

Within this simplified step the oxidation state of the nitrogen goes from $^-3$ in the ammonium to $^+3$ in the nitrite. This has involved the donation of electrons from the nitrogen atom (or oxidation) where oxygen has acted as the electron acceptor (has been reduced). ((Metcalf and Eddy (1991)).

This reaction proceeds through the action of a group of approximately six bacteria commonly referred to as *Nitrosomonas*. These bacteria are chemoautotrophic meaning they obtain their energy and generate their cell tissue from chemical reactions involving inorganic material (Snoeyink and David

(1980)). The bacteria act as catalysts in the reaction by reducing the activation energy required for the ammonium ion to be oxidized (Thain and Hickman (1996)).

The second nitrification step involves the oxidation of nitrite (NO_2^-) to nitrate (NO_3^-) as shown in equation (1.2-2).

Step Two - (Nitrification)

$$400NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195O_2 \xrightarrow{Nitrobacter} C_5H_7O_2N + 3H_2O + 400NO_3^-$$

Oxidation state of nitrogen = $^+3$
$^+3 + ^-4 = ^-1$

Oxidation state of nitrogen = $^+5$
$^+5 + ^-6 = ^-1$

Equation 1.2-2 Second stage of nitrification.

Within this simplified step the oxidation state of the nitrogen goes from $^+3$ in the nitrite to $^+5$ in the nitrate. This has involved the donation of electrons from the nitrogen atom (or oxidation). Again oxygen acts as the electron acceptor.

This reaction proceeds through the action of a group of bacteria, commonly referred to as *Nitrobacter*. These bacteria are also chemoautotrophic. As with the previous stage these bacteria act as catalysts reducing the activation energy required for the reaction to occur.

Note that the term nitritation is often used to refer to the nitrification step from NH_3-N to NO_2-N while the term nitratation refers to the nitrification step from NO_2-N to NO_3-N. It should also be noted that the nitrification process consumes approximately 7.14 grams of alkalinity per 1 gram of ammonia oxidized, thus a pH drop can occur if the wastewater lacks sufficient alkalinity for the nitrification of ammonia to nitrate. From equations 1.2-1 and 1.2-2 it can be seen that

approximately 4.3 mg of O_2 is required for the oxidation of each mg of ammonia nitrogen to nitrate nitrogen. In a biological treatment process additional oxygen would be supplied (by aeration) to the wastewater for these reactions. The research of Painter (1977) found the DO concentration for nitrification should be higher than 2.0 mg/L for nitrification to occur without the availability of oxygen being rate limiting to the process. Bliss and Barnes (1986) found that nitrification ceased to occur at residual DO concentrations below 0.2 mg/L.

It should be noted that the nitrification steps described in equations 1.2-1 and 1.2-2 do not facilitate nitrogen removal from the wastewater but they do eliminate its oxygen demand. However the nitrogen is now in the form of nitrate nitrogen (NO_3-N). To remove nitrogen another step called denitrification is required.

1.3 DENITRIFICATION

Denitrification involves the conversion of nitrate nitrogen (NO_3-N) to nitrogen gases (which are released to the atmosphere). This is accomplished biologically under anoxic conditions by a group of chemoheterotrophic bacteria. Chemoheterotrophic means the bacteria obtain their energy and/or generate their cell tissue from chemical reactions involving organic carbon material (Thain and Hickman (1996)). The denitrifying microorganisms are part of the heterotrophic group of microorganisms that may use oxygen as the electron acceptor in the (biologically catalysed) oxidation of organic substrates. These organisms are facultative in that they can live under altered conditions using either oxygen or nitrate nitrogen as an electron acceptor (Henze (1991)). In an aerobic environment they tend to use oxygen as the preferred acceptor, however when DO concentrations are very low or when only chemically bound oxygen is available (i.e. an anoxic environment) they have the ability to use nitrate nitrogen as an electron acceptor. When anoxic conditions are provided along with an organic substrate (requiring oxidation) this results in the reduction of the NO_3-N to nitrogen gas as electrons are transferred from the substrate to the NO_3-N. It is

thought that the electron transfer pathway for the transfer of electrons from organic material to the electron acceptor is similar regardless of whether oxygen or nitrate acts as the final electron acceptor (Christensen and Harremoes (1977) and Haandel *et al* (1981)).

A simplified illustration of the denitrification reaction is shown in equation 1.3-1.

$$NO_3^- \rightarrow NO_2^- \rightarrow (NO - N_2O - N_2)$$

Equation 1.3-1 Simplified illustration of denitrification reaction.

The last three compounds are gaseous products (nitrogen monoxide or nitric oxide, di-nitrogen oxide or nitrous oxide, and nitrogen gas) that are released to the atmosphere.

The simplified denitrification reaction shown in equation 1.3-1 can be illustrated in an example-using methanol as the carbon source as shown in equations 1.3-2, 1.3-3, and 1.3-4. Equations 1.3-2 and 1.3-3 show the energy creation and growth components of the denitrification reactions with methanol while equation 1.3-4 shows the overall combination of the two reactions (Metcalf and Eddy, 1991). Example, Denitrification (using methanol as the carbon source)

$$6NO_3^- + 2CH_3OH \rightarrow 6NO_2^- + 2CO_2 + 4H_2O$$
$$6NO_2^- + 3CH_3OH \rightarrow 3N_2 + 3CO_2 + 3H_2O + 6OH^-$$

$$6NO_3^- + 5CH_3OH \rightarrow 5CO_2 + 3N_2 + 7H_2O + 6OH^-$$

Oxidation state of nitrogen = $^+5$
$^+5 + ^-6 = ^-1$

Oxidation state of nitrogen = 0

Oxidation state of carbon = $^-2$
$^-2 + ^+3 + ^-2 + ^+1 = 0$

Oxidation state of carbon = $^+4$
$^+4 + ^-4 = 0$

Equation 1.3-2 Energy reaction

$$3NO_3^- + 14CH_3OH + CO_2 + 3H^+ \rightarrow 3C_5H_7NO_2 + H_2O$$

Equation 1.3-3 Biosynthesis reaction

$$NO_3^- + 1.08CH_3OH + H^+ \rightarrow 0.065C_5H_7NO_2 + 0.47N_2 + 0.76CO_2 + 2.44H_2O$$

Equation 1.3-4 Overall reaction

Note in equation 1.3-2 that the oxidation state of nitrogen goes from $^{+}5$ to 0. Therefore the nitrogen atom has accepted electrons or has been reduced. The electrons have come from the organic carbon source. Note also the oxidation state of the carbon has gone from $^{-}2$ to $^{+}4$ i.e. it has donated electrons or has been oxidized.

Until recently denitrification within the wastewater treatment environment was considered as being exclusively anoxic. However it has been found that (under certain conditions) denitrification can occur in aerobic environments. This phenomenon has been called aerobic denitrification.

1.4 AEROBIC DENITRIFICATION

Aerobic denitrification other wise known as simultaneous or co-current nitrification and denitrification (SND) (co-N/DN) implies that nitrification and denitrification occur simultaneously in the same treatment reactor under identical environmental conditions.

Aerobic denitrification has attracted the interest of wastewater treatment plant designers and operators because it offers

1. Potential to save on a second anoxic tank either by a reduction or by the elimination of the need for anoxic facilities
2. May result in a reduction in the treatment time required for a nitrification and denitrification process

3. Potential advantages in terms of energy savings by reducing the aeration requirements required for the oxidation of ammonia nitrogen
4. Potential advantages in terms of reducing the need for variable anoxic/aerobic zones and the associated energy requirements
5. Potential "biological" as well as conventional energy savings. For example, research by Helmer and Kunst (1998) and Stross (2000) suggests that under certain conditions the micro-organisms responsible for aerobic denitrification may be autotrophic. Other research Third (2004) suggests that under certain conditions aerobic denitrification may be undertaken using stored intracellular carbon. If either of these claims are true the need to supply a readily degradable organic carbon source (as a source of electrons/energy) for denitrification may be reduced or overcome. This may allow a reduction in the quantity of flow recycled or the need for an additional external carbon source.

According to the traditional concept of nitrification and denitrification, aerobic denitrification is not possible as nitrification relies on the presence of oxygen where as denitrification requires the absence of oxygen. Initially the denitrification process was thought of as truly anoxic, however from the mid 1980's it was noticed that some full-scale facilities were experiencing nitrogen losses that could not be accounted for by the traditional nitrogen and denitrification concepts. For example a 1985 investigation of a full-scale SBR plant at the Grundy Center WWTP in Iowa revealed the SBR operating without an anoxic or anaerobic phase unintentionally removed approximately 80% of the inorganic nitrogen and over 50% of the phosphorus from the system (Irvine (1987)). The U.S.EPA (1987) reported that total nitrogen losses of up to 30% were frequently occurring in the aeration tanks of many full-scale BNR processes. The documented losses in full-scale facilities were complemented by researchers such as Kugleman and Spector (1988) who identified nitrogen losses from an A/O treatment plant at

Pontiac Michigan in which full-scale aeration tanks reported total nitrogen reductions of 30%.

Other early reports of the existence of aerobic denitrification activity include Moriyama *et al* (1990) who demonstrated aerobic denitrification in biological contactor units and Masuda *et al* (1991) and Gupta *et al* (1994) who demonstrated aerobic denitrification in fixed film RBC units. Halling *et al* (1992) demonstrated aerobic denitrification within up flow fixed bed reactors and Watanabe *et al* (1992) and Munch *et al* (1996) who demonstrated the phenomenon within sequencing batch reactors.

There have been various explanations for the mechanisms by which nitrogen is reduced within aerobic treatment systems to nitrogen gas. These explanations suggest aerobic denitrification is the result of either a biological or a physical phenomenon. It is possible that a number of different processes all contribute in some way to the reduction of oxidized ammonia.

1.4.1 BIOLOGICAL EXPLANATIONS FOR AEROBIC DENITRIFICATION

Biological explanations include microorganisms continuing to use nitrogen after an anoxic phase, microorganisms simultaneously using oxygen and nitrate as receptors, inhibition of oxygen respiration by nitrite resulting in the use of NO_X-N, that traditional BNR theory is too simplistic, and the physiological variety of microorganisms is greater then previously thought.

An early theory proposed by Kugleman and Spector (1988) was that some of the microorganisms responsible for denitrification during an anoxic phase might be able to continue reducing nitrogen for an undefined period once oxygen concentrations had increased i.e. in the aerobic zone/tank following an anoxic period. They found the aerobic denitrification phenomenon seemed to be restricted to the biomass which developed in A/O or anoxic/aerobic style systems. The theory was also indirectly supported by Payne (1981) who found

the denitrifying enzymes of some bacteria were inactivated by oxygen, while in others, synthesis was suppressed, but the existing enzymes disappeared only gradually meaning it might be possible for some denitrifiers to continue denitrifying after an increase in DO concentration. Munch *et al* (1996) suggested that heterotrophic bacteria coming from the anaerobic/anoxic phase might for a limited period still produce enzymes that use NO_x-N as a final electron acceptor even though readily available dissolved oxygen is present. Patureau *et al* (2000) also identified improved aerobic denitrification activity just after an anoxic period and suggested it was due to the "expression of" enzymes synthesized during the anoxic period.

However there have been many instances of the existence of aerobic denitrification in systems that do not contain anoxic or anaerobic environments. Thus while these explanations cannot be ruled out it is now clear that there are also other mechanisms involved. Another explanation for the aerobic nitrogen reduction is the suggestion that it might be possible for some microorganisms to simultaneously use oxygen and nitrate/nitrite as electron acceptors in the oxidation process (Zhao *et al* (1999)).

In the denitrification process nitrate and nitrite generally serve as electron acceptors in the respiratory transport chain in the same way oxygen does in the nitrification process. This is achieved with only a small modification to the metabolic system of the micro-organisms. One explanation for the nitrogen losses is that the acceptance of electrons by the nitrate/nitrite in solution during an aerobic process could result in the transformation of these elements to a gaseous nitrogen form. Some researchers have questioned this explanation on the basis that nitrifiers have been shown to prefer using dissolved oxygen as an electron acceptor even when the dissolved oxygen concentration is as low as 0.1 mg/L (Knowles (1982)). However other researchers such as Kugleman *et al*

(1991) have suggested a possible inhibition of oxygen respiration by nitrite, resulting in the use of NO_x-N as an electron acceptor.

When aerobic denitrification is active the [NO_2-N] is often elevated (Hayward (1998), Yoo *et al* (1999)). This is unusual as the traditional two stage nitrification process is usually rate limited by the oxidation of NH_3-N to NO_2-N resulting in the rapid conversion of NO_2-N to NO_3-N, (and a distinct absence of detectable/measurable NO_2-N). The higher levels of NO_2-N suggest the second step of nitrification (nitration undertaken by *Nitrobacter*) may be inhibited.

Free ammonia or elevated pH levels have been known to inhibit *Nitrobacter,* other inhibitors include reduced temperatures, operating solids content, and acute process loadings (Anthonisen *et al* (1976), Alleman (1984), Abeling and Seyfried (1992), Ballmelle *et al* (1992), Rhee *et al* (1997), Yu *et al* (1998)).

A number of researchers have proposed that nitrogen removal may take place via a shortened nitrite pathway. In some instances this is accompanied by elevated nitrite concentrations. For example Pochana and Keller (1999) conjectured that elevated NO_2-N levels experienced in the aerobic denitrification process may be linked to reduction of nitrogen directly from the NO_2-N form. They found that when nitrification activity in the aerobic denitrification process was inhibited nitrite was not further oxidized to nitrate even after ammonia oxidation was complete. They proposed this situation accompanied a shortened nitrogen removal pathway with the reduction of NO_2-N directly to nitrogen gas. Kim *et al* (2003) demonstrated aerobic denitrification within a biofilm airlift reactor operated specifically under conditions in which low dissolved oxygen created *Nitrobacter* inhibition. Biological nitrogen removal via the nitrite pathway was also demonstrated by Strous *et al* (1997). He identified a bacterium belonging to the Planctomycetes group called ANAMMOX (acronym for Anaerobic Ammonium Oxidation) that could oxidise ammonium anaerobically using nitrite as its electron

acceptor (converting it to dinitrogen gas and trace amounts of nitrate). The ammonium was converted to dinitrogen gas and small amounts of nitrate. Stross (2000) found that ANAMMOX bacteria can be active in the aerobic denitrification process and that under conditions of low dissolved oxygen can reduce nitrite directly to dinitrogen gas. He found that under conditions of low dissolved oxygen concentration traditional nitrifiers such as *Nitrosomonas* and *Nitrosospira* could work cooperatively with ANAMMOX bacteria. That is nitrification was limited to the production of nitrite by *Nitrosomonas* and *Nitrosospira* which was then simultaneously reduced. This is a completely autotrophic process which Dijkman and Strous (1999) named CANON (an acronym for Completely Autotrophic Nitrogen-removal Over Nitrite). The CANON process can be considered in two stages which occur simultaneously, first the oxidation of ammonium to nitrite (equation 1.4-1) and the reduction of nitrite to nitrogen gas (equation 1.4-2). The combined reaction is illustrated in equation 1.4-3.

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

Equation 1.4-1 Half step nitrification reaction under low dissolved oxygen conditions

$$NH_4^+ + 1.3NO_2^- \rightarrow N_2 + 0.13NO_3^- + 2H_2O$$

Equation 1.4-2 Anammox mediated reaction

$$NH_4^+ + 0.85O_2 \rightarrow 0.435N_2 + 0.13NO_3^- + 1.3H_2O + 1.4H^+$$

Equation 1.4-3 CANON reaction – Autotrophic removal of nitrogen under aerobic denitrification conditions

Others to demonstrate denitrification from systems via the nitrite pathway include Yu (1998) who showed denitrification from a continuous flow SBR system in which full pathway nitrification had become fully inhibited, (minimal nitrate was

formed) and Abeling and Seyfried (1992), Yang and Alleman (1992), Akunna *et al* (1993), Ho (1994), Helmer and Kunst (1998), Gejlsbjerg *et al* (1998), and Yoo *et al* (1999) who identified coupled NH_4^+-N oxidation and NO_2-N reduction as an important source of N_2O production under nitrifying conditions in activated sludge.

From the mid 1980's it was also found that nitrate may be reduced under certain aerobic conditions in place of oxygen. Poth (1986), Abeliovich and Vonshak (1992), and Bock *et al* (1995) found that under oxygen limiting conditions some autotrophic nitrifiers were able to reduce nitrate or nitrite into nitric and nitrous oxide and nitrogen gas. More recently Patureau *et al* (1996a) demonstrated co-respiration of oxygen and nitrates through kinetic experiments.

The use of nitrate nitrogen as an electron acceptor (in place of oxygen) may also be considered from a thermodynamic perspective. The potential energy available to microorganisms from the transfer of electrons depends upon several variables including the final electron acceptor. The free energy change ($p\varepsilon^o$) between the use of O_2, NO_3-N, and SO_4^{-2} shows the free energy change available through the use of oxygen is only slightly higher than when NO_3-N is used. This might suggest the O_2 electron acceptance pathway is only slightly preferred over the NO_3-N pathway (i.e. the additional energy available to microorganisms through the use of O_2 as opposed to NO_3-N may not be that significant). The $p\varepsilon^o$ values for O_2, NO_3-N, and SO_4^{-2} respectively are +21.5 , +21, +5.75 (Snoeyink and David (1980)).

Other likely explanations for the occurrence of aerobic denitrification are that the range of microorganisms involved in biological nutrient removal may be of greater physiological variety than previously thought, traditional nitrification

denitrification theory is too simplistic, and some previously identified organisms have a more complex respiratory system than was initially recognized.

In recent years some researchers have suggested the physiological variety of microorganisms involved in biological wastewater nutrient transformation is greater than previously thought. For example Drysdale *et al* (1999) undertook an investigation into the microbial species responsible for denitrification in activated sludge processes and found the microbial consortium was so diverse that he recommended further research to identify constituent bacteria. Delgenes and Patureau (2004a) while investigating the ability of *M. aerodenitrificans* to nitrify and aerobically denitrify attempted to isolate other aerobic denitrifiers, they found many aerobic denitrifying strains. Frette *et al* (1997) isolated one hundred and sixty-nine bacterial strains from an alternating aerobic/anaerobic activated sludge wastewater treatment basin. They found sixteen strains from a sub sample of 23 nitrogen oxide reducers were true respiratory denitrifiers, and all denitrified under both anaerobic and aerobic conditions.

Traditional theory also believed that (for the purposes of wastewater treatment ecosystems) nitrification was undertaken by autotrophic microorganisms under aerobic conditions, and denitrification was undertaken by heterotrophic microorganisms under anoxic conditions. For practical purposes it was believed that dissolved oxygen was the only electron acceptor in aerobic processes, that is other elements such as nitrates could not be reduced in aerobic systems as oxygen was thought to be preferentially reduced. However recent research has shown the traditional theories to be too simplistic, for instance the presence of heterotrophic nitrifiers in wastewater treatment processes has been demonstrated (Verstraete (1975), Castignetti and Hollocher (1984), Kuenen and Robertson (1987), Robertson (1988), Robertson *et al* (1988), Robertson *et al* (1989), Van Niel (1991), Robertson and Kuenen (1992), Van Niel *et al* (1992), and Zhao *et al* (1999)). For example Robertson (1988) and Van Niel (1991)

identified heterotrophic microorganisms able to both nitrify in aerobic environments and denitrify in both aerobic and anoxic environments and Zhao *et al* (1999) found that heterotrophic nitrification could contribute a significant fraction of ammonia oxidation under favorable conditions, such as low dissolved oxygen concentration and relatively high organic loading. It was suggested that autotrophic nitrifiers became inhibited under these conditions. The presence of autotrophic denitrifiers has also been demonstrated Poth (1986), Abeliovich and Vonshak (1992), and Bock *et al* (1995). They identified autotrophic denitrifiers able to reduce nitrate or nitrite into nitric and nitrous oxide and nitrogen gas under conditions of low dissolved oxygen concentration.

Since the mid 1980's it has also become evident that some of the previously identified BNR species have a more complex respiratory system than was initially recognized. For example Robertson and Kuenen (1984) and Lloyd *et al* (1987) demonstrated how traditional nitrifier species such as *Nitrosomonas eutropha* and *Nitrosomonas europea* were able to denitrify in the presence of small amounts of oxygen.

1.4.2 PHYSICAL EXPLANATION FOR AEROBIC DENITRIFICATION

Another explanation is that aerobic denitrification results from anoxic micro zones inside activated sludge flocs (Rittmann and Langeland (1985), Metcalf and Eddy (2001)). This theory suggests that aerobic denitrification is a physical phenomenon that can be explained using the traditional concepts of autotrophic nitrification on the exterior of sludge flocs and heterotrophic denitrification using adsorbed organic carbon within an anoxic micro zone at the centre of the sludge floc. The corner stone to this theory is the belief that denitrification could occur within flocs due to a dissolved oxygen concentration gradient within the floc as shown in Figure 1.4-1.

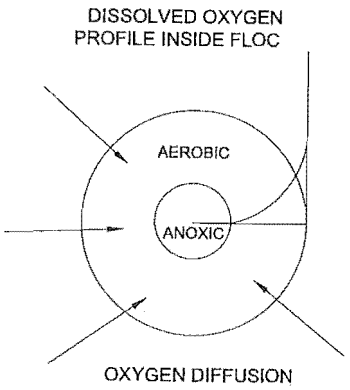


Figure 1.4-1 Schematic of possible dissolved oxygen profile within microbial floc (Adapted from Pochana and Keller 1999).

Typical floc sizes within the activated sludge process were found to range from 5-200 µm in diameter by Andreadakis (1993), 10-70 µm by Pochana and Keller (1999), and 50-110 µm Third (2004). The floc diffusion theory was tested by Pochana and Keller (1999) who illustrated that a reduction in median floc size from 80 to 40 µm by high speed blending of the biomass before a cycle resulted in a reduction in aerobic denitrification nitrogen losses from 52 to 21 %. This occurred while nitrification rates remained constant suggesting that the drop in aerobic denitrification was not due to blending operations affecting the viability of the biomass. The studies suggested that floc size may play an important part in aerobic denitrification activity. Pochana *et al* (1999) also developed a mathematical model to simulate internal floc diffusion mechanisms and found that while the outer part of flocs had a DO level above 0.2 mg/L (thereby reducing denitrification activity) the central sections of flocs had considerable time with virtually no DO providing an environment suitable for anoxic reduction to occur. This finding supported the theory that aerobic denitrification may be partly attributed to traditional denitrification within sludge flocs.

From a full-scale perspective it has been reported that the Potsdam wastewater treatment plant in Germany (90,000 p.e.) achieves aerobic denitrification via

internal floc denitrification. Demoulin *et al* (2001) illustrated how the plant used online measuring of the specific oxygen uptake rate to control the aerobic denitrification process. Typical floc profiles were as illustrated in Figure 1.4-2. They found the rate of nitrate diffusion into the floc was on the order of ten times that of oxygen, thus under aerated conditions there was no nitrate limitation within the floc. They also reported that sufficient carbon provision for denitrification was achieved through carbon storage (biosorption) and the control of dissolved oxygen which minimized the use of substrate carbon by oxic metabolism.

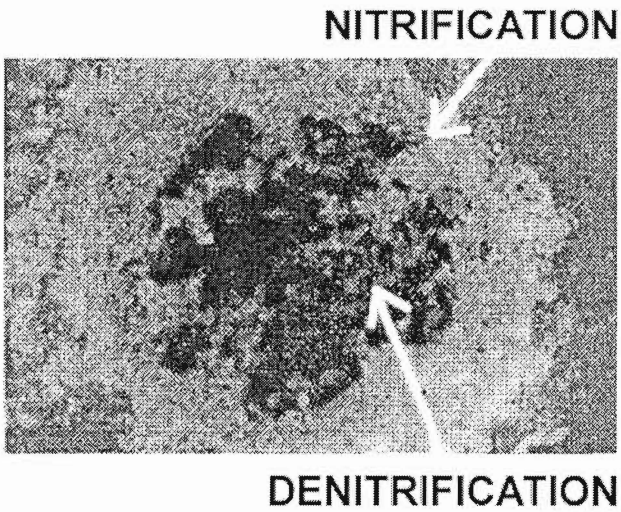


Figure 1.4-2 Representative view of sludge floc under a microscope with suggested zones for nitrification and denitrification. (Adapted from Demoulin *et al* (2001)).

Heinen and Norgaard (1998) reported on the application of floc diffusion theory to the full-scale "Symbio process". The Symbio process is a nitrogen removal technology which has been developed on the basis of using dissolved oxygen concentration gradients within microbial flocs, The process attempts to maintain aerobic and anoxic zones within flocs through the control of a number of biological parameters (mainly low dissolved oxygen concentration).

The floc oxygen diffusion theory may be indirectly supported by a number of researchers (refer discussion 5.4) who have suggested the optimum dissolved oxygen concentration for aerobic denitrification would be around 0.5 mg/L. The general consensus is that the process has an upper limit of around 1.0 mg/L and an optimum just under 0.5 mg/L. It should be noted these are theoretical values, a review of the literature found no research that has experimentally determined the optimum dissolved oxygen concentration range for the aerobic denitrification process.

However the floc diffusion explanation has also been questioned by a number of researchers including Helmer and Kunst (1998) who achieved significant aerobic denitrification nitrogen losses in a reactor (with dilute mechanically homogenized biomass) in which large cell clusters were eliminated ensuring all cells were supplied equally with DO during batch tests. The earlier research of Kugleman *et al* (1991) also creates some doubt as to the degree of nitrogen loss that can be attributed to anoxic micro zones within flocs. In a lab scale (A/O) type process with significant aerobic nitrogen losses they increased the DO concentration to a constant 10 mg/L in order to reduce the volume of any possible anoxic/anaerobic micro zones within the interior of floc particles. After 14 days of operation the aerobic nitrogen losses were identical to the losses they experienced while operating at 5 mg/L (around 30%). Kugleman *et al* (1991) supported their findings with research undertaken by Robertson and Kuenen (1984) and Kawakami *et al* (1985) who both established aerobic denitrification within pure cultures maintained under highly aerobic conditions. Patureau *et al* (1996b) also demonstrated simultaneous nitrate and oxygen reduction within a chemostat culture maintained under conditions of high dissolved oxygen. The floc diffusion theory may also be questioned by the work of Bang *et al* (1995) who studied aerobic denitrification activity in the biofilms attached to a partially submerged RBC, they found the numbers of denitrifiers in the surface layer of the biofilm

were of 1 to 2 orders of magnitude higher than those in the middle and bottom layers. From this they suggested the surface layers had a higher denitrifying activity. They also found aerobic denitrification was active at dissolved oxygen concentrations up to 6 mg/L.

It is clear that to date, no definitive explanation for the loss of nitrogen under aerobic conditions has been agreed upon. It is likely that aerobic nitrogen losses may be the result of a number of mechanisms such as biological conversion by a broad range of microorganisms under a range of conditions, as well as traditional biological conversion resulting from a physical phenomenon such as anoxic micro zones contained within flocs. As to the debate over the conditions required for aerobic denitrification the generally accepted consensus is that aerobic denitrification is principally a low dissolved oxygen concentration process ($\leq$ 1.0 mg/L), the optimum dissolved oxygen concentration range for aerobic denitrification has not been determined experimentally. The requirements for organic carbon remain unclear.

The measurement of biochemical parameters such as dissolved oxygen and pH is important for control and monitoring of the nitrification, denitrification, and aerobic denitrification processes, this is typically achieved using insitu probes.

1.5 OPERATION OF PROBES

The commonly used insitu control parameters for activated sludge are ORP (Oxidation Reduction Potential), DO (Dissolved Oxygen) and pH as the probes are inexpensive and easy to use (Peng *et al* (2002)). In this research all measurements for ORP, pH, and DO have been undertaken using probes as follows:

1.5.1 OXIDATION REDUCTION POTENTIAL (ORP)

ORP cannot be determined experimentally, rather it is always measured using an ORP probe. The measurement of ORP allows the ratio of oxidants to reductants prevailing within a solution to be established. The actual redox potential of a solution may be considered as the tendency to give up or take up electrons (i.e. to be oxidized or reduced).

The ability of a solution to give up or take up electrons can be measured by immersion of a platinum electrode along with a reference electrode (such as Ag/AgCl). Figure 1.5-1 provides an illustration of an ORP probe and its components. When the probe is immersed into a solution the flow of electrons (in an attempt to create an equilibrium) results in a measurable millivolt difference between the two electrodes.

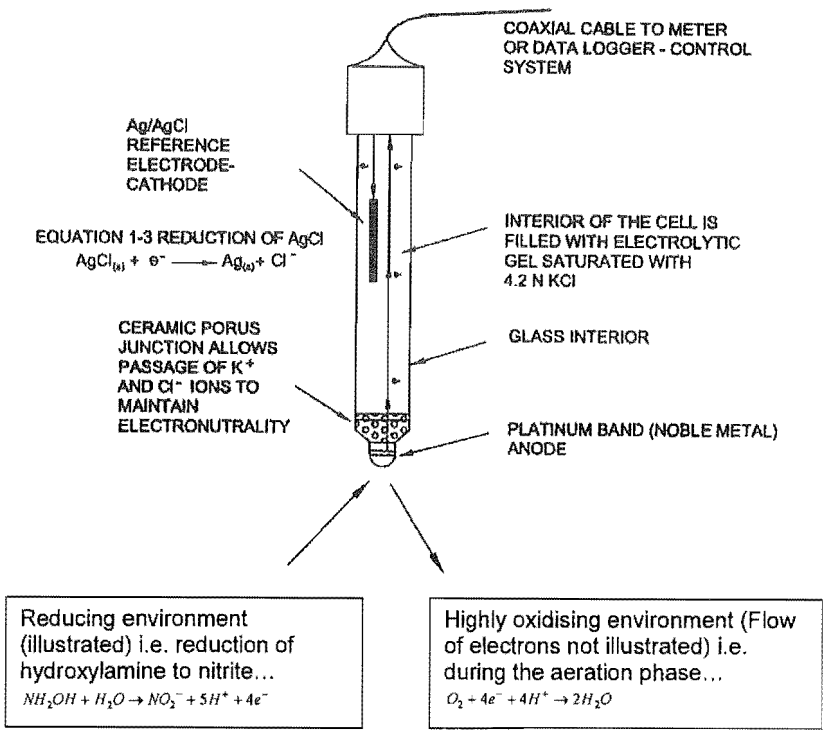


Figure 1.5-1 Diagram of an ORP electrode and operation

To illustrate, within a denitrification process, there is a lack of freely available dissolved oxygen. Organic material within this environment is continuously subjected to degradation by redox reactions catalyzed by enzymes. The organic material is oxidized in that it donates electrons and these electrons are accepted by nitrate nitrogen which is itself reduced to nitrogen gas. When an ORP probe is in this solution some of the electrons from the oxidized organics will gravitate along the platinum wire to the electrode (cathode) since the Ag/AgCl reference electrode has a large positive electrode potential. The flow of electrons will cause the Ag/AgCl to be reduced forming solid silver and free chloride irons. In this environment when the flow of electrons is from the solution to the reference electrode the recorded ORP value will be negative. Thus a reducing environment (i.e. during an anoxic phase) will cause the ORP mV reading to fall or have a negative slope over time (BIOLAB Scientific (2003)).

When oxygen is present in solution the oxygen has a larger positive potential than the reference Ag/AgCl electrode. That is the electrons from the oxidation of materials such as organic carbon and ammonia which would have traveled to the reference electrode will instead travel to the oxygen (and reduce the oxygen to water). Thus material such as organic carbon and ammonia nitrogen are oxidized and donate electrons while oxygen is reduced or accepts electrons. In addition the oxygen has a greater attraction for electrons than the probe's Ag/AgCl electrode and this results in a flow of electrons from the electrode to the oxygen in solution. When the flow of electrons is from the reference electrode to the solution the recorded ORP value will be positive. Thus an aerobic environment (i.e. during an aeration phase) will cause the ORP mV reading to increase or have a positive slope over time (BIOLAB Scientific (2003)).

1.5.2 HYDROGEN ION CONCENTRATION (pH)

The pH can be determined experimentally but is usually measured with a pH probe. The inside of a pH probe contains a HCl solution of fixed $[H^+]$ which acts as one half of a cell, the other half of the cell being a reference electrode

composed of material such as Ag/AgCl. The probes have a thin glass (bulb shaped) membrane located at the tip. The glass membrane separates the internal HCl solution from the material being measured but allows an H^+ ion exchange to take place. The electrode works by allowing hydrogen ions to exchange at the glass surface. The flow of H^+ between the internal solution and the solution being measured changes the Cl^- concentration in the HCl solution. This is in turn balanced by the Ag/AgCl electrode. Equation 1.5-1 illustrates the action of the Ag/AgCl reference electrode depending upon the Cl^- concentration in the probe HCl solution.

$$AgCl_{(s)} + e^- \Leftrightarrow Ag_{(s)} + Cl^-$$

Equation 1.5-1 Action of reference electrode

The Ag^+ ion either forms an ionic bond with the Cl^- ion or alternatively can accept one electron to balance its valence charge. Thus there is a flow of electrons similar to the situation described for the ORP probe (Snoeyink and David (1980), Tchobanoglous and Schroder (1987), Oxford dictionary of chemistry (1996)). Readings of the electron flow can be made on a high resistance voltmeter or pH meter (which is essentially a high resistance voltmeter with a scale to read in pH). This reading can be used to determine the difference between the constant internal $[H^+]$ and the external variable $[H^+]$. An illustration of a pH probe is provided in Figure 1.5-2.

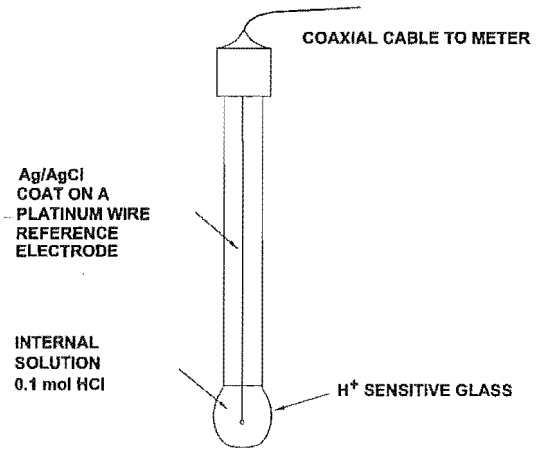


Figure 1.5-2 Diagram of a pH electrode

1.5.3 DISSOLVED OXYGEN CONCENTRATION [DO]

The dissolved oxygen concentration within a solution can be measured experimentally via chemical titration or alternatively using a DO probe and meter. A DO probe contains a sensor which is surrounded by KCl solution. A membrane separates the sensor from the solution being measured. Dissolved oxygen is free to pass from the solution being measured into the probes KCl solution. A DO meter is able to take a reading by passing a polarizing voltage across the sensor, this causes oxygen which has passed through the membrane to react at a cathode causing a current to flow. The membranes and KCl solution are disposable and usually require replacement every week if the probe is used continuously. For low dissolved oxygen measurements such as in the aerobic denitrification process thin membranes can be used which allow increased sensitivity and greater accuracy of measurement (BIOLAB Scientific (2003)).

The output from probes such as dissolved oxygen, oxidation reduction potential, and pH may be logged. When plotted over time the data produces curves known as profiles. If plotted in real time the data produces online real time profiles.

1.6 ONLINE REAL TIME PROFILES (ORT PROFILES)

The present research used four online parameters, these were oxidation reduction potential (ORP), pH, dissolved oxygen concentration [DO], and air demand. Figure 1.6-1 illustrates a generalized schematic of the online profiles that could be expected from an A/O process treating domestic wastewater (note the air demand profile is not illustrated).

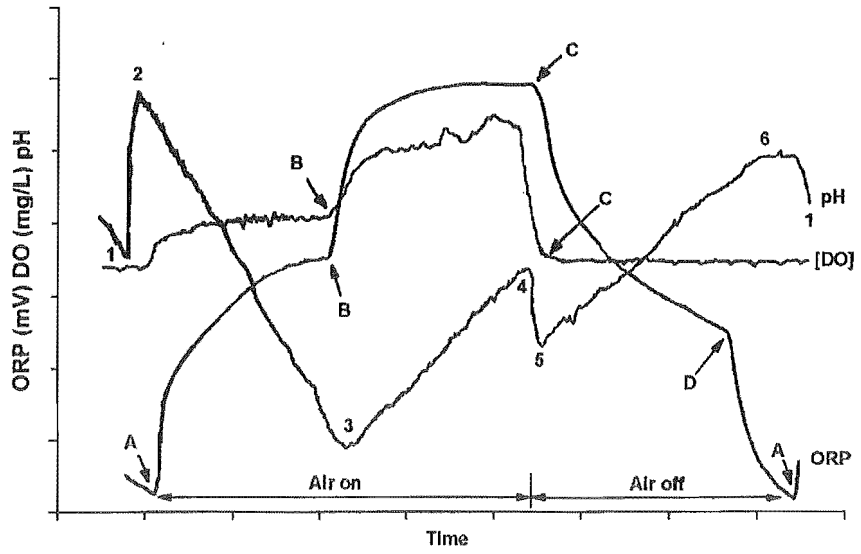


Figure 1.6-1 Generalized schematic of ORP, pH, and DO profiles, main bending points illustrated.

The profiles contain features that correspond to changes in biochemical conditions. These features are of interest as they indicate when certain events have occurred and can provide insight into the treatment process. To understand the use of real time parameters it is necessary to have knowledge of the various features, thus the following section will provide some background information to this end.

With respect to the ORP profile in Figure 1.6-1, the ORP profile has four main bending points; these are labeled A, B, C and D respectively, (note that bending points B and C also appear on the DO profile).

At point A the air is switched on which causes the ORP to change from a negative (downward facing) slope to a positive slope, (i.e. as discussed in section 1.5.1 electrons start flowing from the ORP electrode to the oxygen in solution). The strong attraction of oxygen for electrons results in an interrelationship between the ORP and DO profiles. ORP is linked to dissolved oxygen concentration (or any electron acceptor/donor for that matter) by a logarithmic relationship (Paul *et al* (1998)). Thus the change in ORP is not proportional to electron acceptor concentration but the log of its concentration. This means that large changes in concentration result in small changes in redox potential (Mosey (1985)).

For a nitrification type process the ammonia nitrogen concentration will be depleted after a certain aeration period. Point B is thought to occur when the ammonia nitrogen is exhausted resulting in the elbow feature on both the dissolved oxygen and the ORP profile, (often referred to as the "ammonia elbow" Yu *et al* (1998), Ra *et al* (2000), Holman and Wareham (2003)). Dissolved oxygen breakthrough typically occurs at point B as oxygen is no longer required to act as an electron acceptor for ammonia. This means that additional oxygen is available to accumulate and this increases the residual dissolved oxygen concentration. Note that the logarithmic relationship between DO and ORP means that under conditions of high dissolved oxygen concentration a small variation in the dissolved oxygen concentration may not be reflected on the ORP profile, thus point B will only be clearly shown on the ORP profile if the oxygen concentration is relatively low (~ < 2 mg/L).

The logarithmic relationship between the dissolved oxygen concentration and ORP allows the bending point B on the ORP profile to be used to indicate whether the aeration rate is appropriate for the oxygen demand. That is the appearance of the ORP bending point typically indicates the oxygen supply rate is suited to the oxygen requirements at that time. Under aeration will result in the dissolved oxygen not breaking through in the aeration time of the process (which means point B does not appear) while over aeration will also result in Point B not appearing on the ORP profile. The absence of point B can also indicate problems with the nitrification process, such as nitrification inhibition (Paul *et al* (1998)).

Once aeration is terminated the dissolved oxygen concentration starts to fall rapidly as biological activity consumes the remaining residual dissolved oxygen. Once the freely available dissolved oxygen is fully depleted the system makes the transition from using dissolved oxygen to using chemically bound oxygen, that is the system goes from aerobic to anoxic activity. At the point where the system becomes anoxic the ORP changes from a relatively level plateau to a steep negative slope (illustrated in Figure 1.6-1 as point C). The flow of electrons changes due to the shift to a reducing environment, that is electrons start flowing to the ORP cathode. It should be noted that this part of the ORP profile effectively represents the actual respirometric activity of the sludge and ORP will decrease strongly only when dissolved oxygen has been consumed completely (Zipper *et al* (1998)).

In the anoxic environment, nitrate nitrogen is reduced to nitrogen gas. The nitrate acts as the electron acceptor (is reduced) while organic carbon is oxidized (donates electrons). Once the NO_x-N is depleted there is a transition from anoxic to anaerobic conditions. At this point the bacteria pass from highly efficient respiration (i.e. using nitrate as a terminal electron acceptor in the electron transport chain) to less efficient (e.g. anaerobic fermentative) processes (Wareham *et al* (1993), Plisson-Saune *et al* (1996)). This transition from anoxic to

anaerobic conditions results in a nitrate breakpoint feature (Peng *et al* (2002), Cecil (2003)). This is illustrated as point D on Figure 1.6-1 and also in more detail in Figure 1.6-2. The nitrate breakpoint feature is often called the "nitrate knee" and it signals the point where the denitrification reaction is complete (i.e. all nitrates have been eliminated).

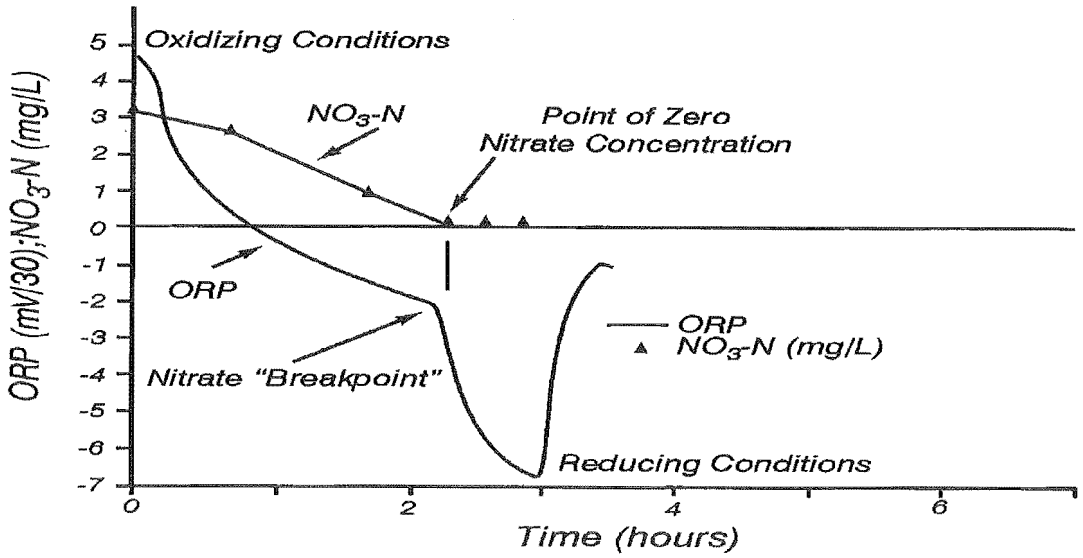


Figure 1.6-2 Typical ORP vs time profile showing nitrate breakpoint (adapted from Wareham *et al* (1993))

Points B and D (Figure 1.6-1) are of particular interest to those working with online real time systems as they represent the points at which nitrification and denitrification (respectively) are complete. Identification of these points can potentially allow treatment sequences to be terminated resulting in benefits such as savings in aeration, greater treatment capacity, and improved process stability.

With respect to the pH profile on Figure 1.6-1, the profile has 6 main bending points or features that are correlated to changing biochemical conditions. At the start of aeration there is typically a sudden sharp rise in the pH (points 1-2). This

is thought to be due to CO_2 stripping from the system caused by the initiation of aeration (Hao and Huang (1996)). After the initial increase the pH decreases again (points 2-3), as nitrification consumes alkalinity as part of the nitrification process (7.14 mg HCO_3 consumed per mg of ammonia). At point 3, the pH curve shows the feature termed "ammonia valley" (Andreottola *et al* (2001)) Point 3 occurs when ammonia is essentially depleted (and nitrification is complete), note that point 3 corresponds to point B on the ORP profile.

Following the ammonia valley at point 3 continued aeration will result in an increase in the pH (points 3-4). Hao and Huang (1996) found that the mechanism behind this increase in pH was complex and not fully understood. They suggested it may be caused by the hydrolysis (or cleavage of organic nitrogen molecules with water) of organic nitrogen after the exhaustion of the ammonia.

For a short period following the termination of aeration the pH can fall. This occurs as the stripping of CO_2 from the system (caused by aeration) ends and there is an increase in the CO_2 concentration (points 4-5) which may occur until anoxic conditions develop. Once the conditions are anoxic the pH increases again as alkalinity (consumed during nitrification) is partially released back into the environment (points 5-6). The increase in pH occurs until denitrification is complete, i.e. all nitrates have been reduced to nitrogen gas. At this point there is a pH breakpoint commonly referred to as the "nitrate apex", (point 6) (Peng *et al* (2002)). The nitrate apex is related to the ORP "nitrate knee" in that it signifies the point at which all nitrates have been depleted and the system makes the transition from anoxic to anaerobic conditions.

Following the nitrate apex the pH profile tends to plateau and then decrease again as anaerobic conditions develop (Points 6-1). Anaerobic conditions occur in three main stages, hydrolysis, acidogenesis, and methanogenesis. Acidogenesis results in the breakdown of products into simple organic acids, the

most common of which is acetic acid. The breakdown of products into organic acids results in the fall in pH observed between points 6-1.

Points 3 and 6 are of particular interest to those working with online real time systems as they represent the points at which nitrification and denitrification (respectively) are complete. As with the ORP features the identification of these points can potentially allow treatment sequences to be terminated resulting in benefits such as savings in aeration, greater treatment capacity, and improved process stability.

1.7 APPLICATION OF ONLINE PARAMTERS

Stricter wastewater effluent requirements and issues such as conservation of energy and a limitation on the available area for treatment facilities has emphasized the need for incorporating new technology into wastewater treatment processes in order to increase their performance (Peng *et al* (2002)). The move towards greater efficiency may be considered both in terms of greater pollutant removal but also in terms of regulating plants to ensure optimum performance in terms of real time pollutant concentrations and hydraulic loads, that is to minimize inefficiencies caused by plants designed for operation at a static design load (Risholt *et al* (2002), Baeza *et al* (2002)). In the last few decades the establishment of international commissions has resulted in the implementation of new wastewater treatment regulations within the European Union (EU). These regulations have drastically increased the need for real time monitoring systems within European wastewater treatment plants (Gunatilaka and Dreher (2003)). Regulatory authorities are now frequently requiring biological nutrient removal (BNR) strategies to be implemented at wastewater treatment facilities, for example new regulations within parts of the EU require nitrogen removal as a treatment objective. Common nitrogen removal requirements (such as those required in Austria) include 60-70% nitrogen removal (BGBl 210/1996) with a decrease in NH_4-N and NO_3-N to below 10 mg/L (Fuerhacker *et al* (2000)).

There is also a growing need within the EU for improved online real time control systems to monitor and control pollution in rivers and water bodies into which treated wastewater is discharged, that is to monitor and take into account pollutant emissions when determining control strategies for minimizing the impact of compounds such as ammonia nitrogen on urban water bodies (Meirlaen *et al* (2002), Frehmann *et al* (2002)). Online real time control strategies are a way of achieving the new treatment objectives and facilities such as new BNR plants offer the opportunity to incorporate real time control as part of the plants ICA system (Cecil (2003)).

pH is an established form of online measurement often used in the wastewater treatment industry to pinpoint the end of nitrification by identifying the ammonia depletion breakpoint (Al-Ghusain *et al* (1994), Al-Ghusain and Hao (1995), Ra *et al* (2000), Andreottola *et al* (2001)). ORP is also an established form of online measurement used to pinpoint the end of denitrification ((Koch *et al* (1985), Wareham *et al* (1993), Yu *et al* (1997a), Charpentier *et al* (1998), Yu *et al* (1998), Peng *et al* (2002), Cecil (2003)).

pH and ORP have shown themselves to be low maintenance, reliable, and relatively inexpensive when incorporated as process control tools in wastewater treatment processes. The probes are not particularly sophisticated and not usually associated with the number of practical problems that can be encountered with the use of sophisticated sensors in the harsh and dirty conditions of a wastewater treatment process (Vanrolleghem and Lee (2003)). Alternatives such as the latest biosensors can have life times as short as 6 weeks and are highly dependent upon variables such as effective sterilization during construction and can be susceptible to mechanical damage (Nielsen *et al* 2002)).

ORP measurement was first used in wastewater treatment from the early 1940's following the development of practical ORP electrodes for this application (Rohlich (1948)). However with the subsequent development of the dissolved oxygen electrode engineers and plant operators lost interest in redox (Cecil (2003)). Interest in ORP was revived when nutrient removal became an objective in the 1980's (Koch (1985)). Nutrient removal required the inclusion of treatment phases in which no dissolved oxygen was present. The profiles from pH, and ORP can operate in anoxic and anaerobic conditions and have the capacity to provide useful information under these conditions with respect to nitrogen transformation and removal. This is primarily because in low dissolved oxygen and/or anoxic-anaerobic environments significant changes in pH and redox potential can occur while conventional control parameters such as the dissolved oxygen probe may show little or no change.

The use of the ORP profile in aerobic-anoxic-anaerobic conditions is illustrated in Figure 1.7-1. The figure shows aeration/non-aeration phases of an A/O type BNR plant. From the start of aeration the ORP profile increases steadily until aeration is terminated after which the ORP decreases. While the operating range of the dissolved oxygen probe stops when the dissolved oxygen is depleted the ORP profile continues providing information during the anoxic-anaerobic reducing conditions. pH and ORP have now become promising contenders for the automated control of process trains that incorporate a micro/non-aerated zone.

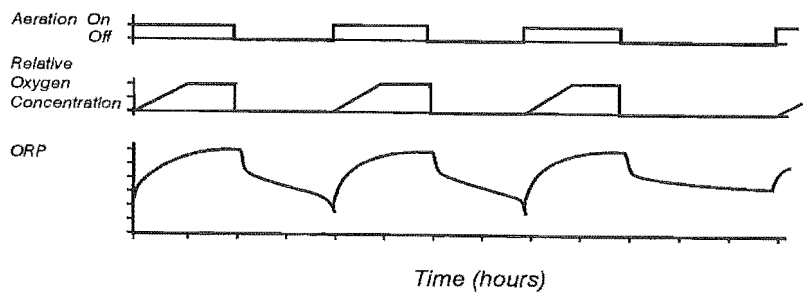


Figure 1.7-1 Typical ORP profile for A/O BNR plant (adapted from NZWWA, 1997)

The use of pH and or ORP profiles for control purposes requires the online data to be analyzed so that process control decisions can be made. Specific profile features are correlated to known biochemical events, when these profile features appear their detection by a control system provides an indirect way of identifying when the biochemical event has occurred. Control decisions can be based upon either the use of set point (absolute) values (that is using set points at which the event is thought to occur) or relative values. Relative values involve measurement of the profile slope so that changes in slope can be used to identify the feature.

Profile features may be considered relative in the sense that different probes may show the breakpoints (features) occurring at different absolute values due to irregularities in the mixing regime, individual probe characteristics, and localized oxidation-reduction reactions occurring in the vicinity of the tip of the probe (ORP). However most probes will tend to show the breakpoints occurring at the same moment in time.

Initial concerns regarding the usefulness of ORP measurements in biological systems Stumm (1966), Morris and Strumm (1967) and Harrison (1972) have been alleviated in light of the knowledge that the emphasis in some situations can be transferred from the absolute ORP value to the relative ORP value (i.e. the ORP variation with time or dORP/dt).

The use of relative ORP variations to monitor nutrient depletion has been demonstrated by numerous researchers including Charpentier *et al* (1989), Peddie *et al* (1990), Wareham *et al* (1994), Paul *et al* (1998), and Ra *et al* (2000). For example Ra *et al* (2000) operated a two stage sequencing batch reactor treating piggery wastewater and used relative ORP to detect the point of nitrate depletion via identification of the nitrate knee feature. The change in slope

or derivative of the ORP profile has also been employed in some modern process control systems and aspects such as the nitrate knee are now being regularly detected by on-line systems which use the information in real time to make changes to the process control (i.e. initiation or termination of aeration). For example, the recent adoption of the nitrate knee in the Zullig ORP control system is reported to provide savings in energy of up to 30% over a strictly timer-based system (Water and wastes in NZ (1997)).

The use of relative pH or pH and ORP variations to monitor nutrient depletion has also been demonstrated by numerous researchers including Al-Ghusain and Hao (1995), Yu *et al* (1997), Kim and Hao (2001), and Peng *et al* (2003). For example Peng *et al* (2003) investigated the variation of pH with time during a nitrification process treating brewery wastewater. They attempted to use the pH ammonia valley to determine the point of ammonia depletion. Kim and Hao (2001) operated an alternating aerobic-anoxic continuous flow activated sludge process and used relative pH to detect the point of ammonia depletion via the ammonia valley and relative ORP to detect the point of nitrate depletion via the nitrate knee.

Aspects such as the application of online parameters for monitoring and possibly control of the aerobic denitrification process, the optimum dissolved oxygen concentration, and the requirements for organic carbon are some areas that require further research and clarification.

1.8 PROJECT NEED, OBJECTIVES, AND METHODOLOGY

1.8.1 PROJECT NEED

To date, little research has been undertaken in the area of ICA (Instrumentation control and automation) or real time control of the aerobic denitrification process. Exceptions include Zhao *et al* (1999) who used absolute ORP as a real-time control parameter for aerobic denitrification, Demoulin *et al* (1997) who illustrated

how ORP measurement and its rate of change throughout a cycle could successfully control dissolved oxygen set points as well as optimize nitrogen and phosphorus removal in a full-scale aerobic denitrification sequencing batch reactor facility, Holman (2000) who investigated online ORP and DO profile features within the aerobic denitrification process and highlighted possible features for process control, and Third (2004) who used online OUR measurements as a process control parameter for the aerobic denitrification process.

A review of the literature suggests there is still a need to experimentally determine the optimum dissolved oxygen concentration for the aerobic denitrification process. It is likely the optimum dissolved oxygen concentration for aerobic denitrification will not be a fixed value but an optimum range dependent upon variables such as the wastewater composition and the biomass concentration.

The requirements for organic carbon in the aerobic denitrification process needs to be clarified. For example the removal of nitrogen via autotrophic denitrification (including aerobic denitrification) was identified in 2002 as an area that requires further research by WG 4 biological processes (working group 4) a division of COST (European cooperation in the field of scientific and technical research) (Cost (2003)).

1.8.2 PROJECT OBJECTIVES

The objectives of this work were to elucidate some operational aspects of the aerobic denitrification phenomenon (relative to alternative traditional separate stage processes). That is to provide some comparisons on aspects such as nitrification, denitrification, and sludge production rates. To comment on the effect of dissolved oxygen concentration and the need for organic carbon, and to

investigate opportunities for several types of real time control (ORP, pH, DO, and airflow).

To achieve this the experimental work had the following specific objectives:

1. Confirm the presence of aerobic denitrification activity
2. Elucidate some operational aspects of aerobic denitrification, in particular comment on the nitrification, denitrification, and sludge production rates
3. Comment on the requirements for air relative to conventional separate stage nitrification denitrification processes
4. Identify the dissolved oxygen conditions necessary for aerobic denitrification and for its optimisation
5. Comment on the need for soluble organic carbon for the removal of nitrogen in the aerobic denitrification process
6. Confirm if the online profiles have unique features with respect to the aerobic denitrification process, in particular the ammonia elbow on the ORP profile and the ammonia valley on the pH profile. Correlate these online features with measured biochemical events such as the depletion of organic carbon or ammonia nitrogen
7. Develop and demonstrate control algorithms that use online features to control the aerobic denitrification process, (i.e. indirectly detect the biochemical events). In doing so demonstrate the reliability of pH and ORP control algorithms based upon relative rather than absolute values

1.8.3 PROJECT METHODOLOGY

Lab scale sequencing batch reactors were operated treating domestic wastewater under conditions likely to produce nitrification and aerobic denitrification.

An intensive chemical parameter testing program (series of track studies) was undertaken along with on-line monitoring of ORP, pH, DO, and air demand to provide real-time analysis of process conditions. Specific cycles were singled out for intensive testing of parameters such as COD, TN, NH_3-N, NO_2-N and NO_3-N. Samples for each of the parameters were taken periodically throughout a cycle. The track studies provided an indication of the presence of aerobic denitrification activity (in the event that a loss of NH_3-N occurred without a corresponding increase in NO_2-N or NO_3-N, once nitrogen assimilation had been considered).

Following the confirmation of the presence of aerobic denitrification activity, its performance was monitored as the operational dissolved oxygen concentration was decreased.

The automatic collection of probe readings at intervals of up to sixty seconds provided real-time profiles rich in information. The outputs from the probes were used for analysis of both trends and specific biological events.

Finally the research attempted to correlate online features with biochemical events and to develop control routines which used these features.

Chapter 2 EXPERIMENTAL HARDWARE AND OPERATION

2.1 REACTORS

Biological treatment of the wastewater was undertaken in two sequencing batch reactors (SBRs). Figure 2.1-1 illustrates a schematic of a reactor.

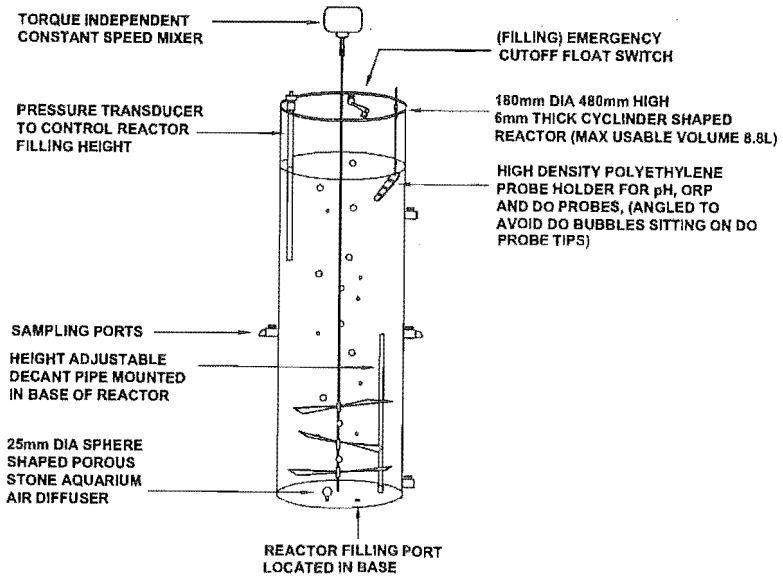


Figure 2.1-1 Diagram of one sequencing batch reactor

The reactors were built with the intention of using one reactor as a control, however the consistency of the treatment process (from the perspective of online readings and biochemical parameter testing) led to the decision to run the reactors independently.

After reviewing various reactor materials (e.g. glass) the decision was made to construct the reactors from 6mm thick perspex. This material was chosen for its high impact resistance and because it was transparent. Transparency was important to allow visual monitoring of the biological process and the assessment of aspects such as flocculation and sedimentation. Other components within the reactors were made from stainless steel, brass, or polyethylene. This eliminated

the use of materials which may have degraded in the potentially corrosive reactor environment.

The decision was made to construct the reactors following similar designs used by other researchers (Munch *et al* (1996), Yu *et al* (1998), Andreottola *et al* (2001), Peng *et al* (2002)). The size of the reactors was based upon the likely cycle lengths and the quantity of feed that could be stored in a modified freezer. As the Christchurch City wastewater treatment plant was 20 km away it was decided the design should not require the collection of feed more than once per week. The usable freezer storage volume was about 450 L, with two reactors this limited the design to a maximum through flow of about 225 L per week per reactor (refer Appendix B2 for design details).

Mixing was undertaken by mixing blades. The motors that turned the mixing blades were required to operate up to 20 hours per day, 7 days per week. Stepper motors were used as they did not contain armature brushes which could have worn out with continuous use. In order to overcome any overheating problems the stepper motors were mounted in aluminum cases with thermally conductive paste, (allowing the motor case to act as a heat sink). In addition a secondary cooling fan was also incorporated within the motor case to provide forced cooling. The use of stepper motors also provided the added benefit of being torque independent, i.e. the RPM was constant regardless of the torque experienced allowing for constant mixing.

Simple, open-shut, solenoid valves (230 volt) were used for control of clarified effluent decanting. The solenoids were normally shut but would open upon supply of 230 volts from the process control system.

Aeration of the activated sludge within the reactors was provided by compressed air sourced from the laboratory reticulated air supply. A single air diffuser was mounted in the base of each reactor.

2.2 AIR SUPPLY SYSTEM

Supply of air to the reactors was necessary for the aerobic period in which carbon, ammonia, and nitrite nitrogen were all oxidized. The reactors were operated at various dissolved oxygen set points (DOSP) from 4.0 mg/L to 0.5 mg/L. For the dissolved oxygen set points from 4.0 mg/L to 1.0 mg/L an aeration system was developed as illustrated in Figure 2.2-1.

The upstream side of the aeration system started with a regulator to reduce the mains air pressure from 80 PSI to 40 PSI allowing for pressures within the range specified by manufactures of the downstream equipment (such as variable rate solenoids and air flow meters. The regulator was followed by a Burket 0-10 Bar 230 Volt on/off solenoid and then a Burket variable rate solenoid, (Burket 0-9 L/min, 0-20mA, 0-2.8 Bar Model 6021). The purpose of the first on/off solenoid was to remove air pressure from the variable rate solenoid when the air supply was off.

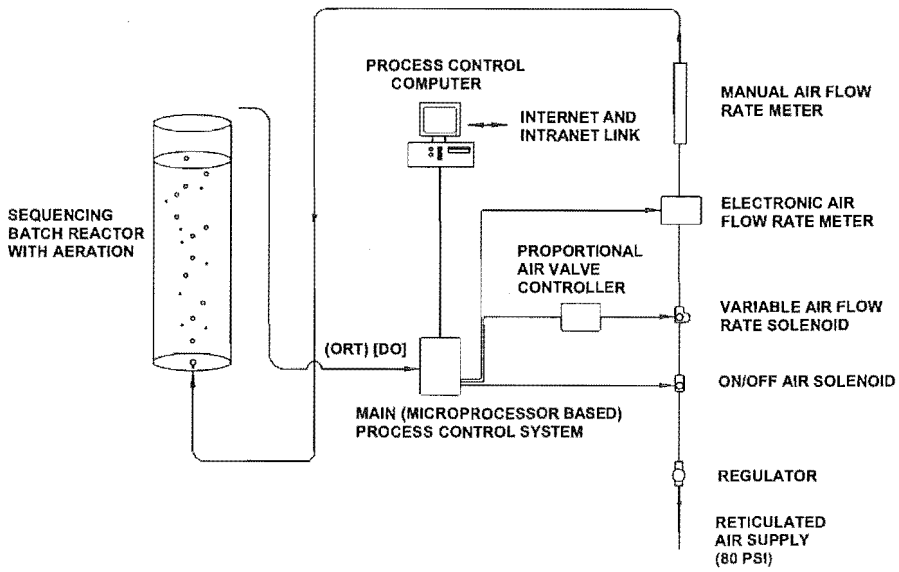


Figure 2.2-1 Aeration system for set points down to 1.0 mg/L (Duplicated for second reactor).

The variable rate solenoid was opened and closed by the proportional air valve controller which determined the difference between the actual dissolved oxygen concentration within the reactor and the desired concentration (specified in the process control software). This difference corresponded to the degree to which the air valve would open. As the difference became smaller the valve would slowly close. Readings were updated every six seconds thereby allowing responsive accurate control of the reactors dissolved oxygen concentration.

Downstream from the variable air flow rate solenoid there was an electronic Honeywell mass air flow sensor. The flow rate sensor was a Model AWM5000 micro switch series/micro bridge able to detect flow accurately between 0-20 L/min. The electronic flow rate sensor was linked to the process control system and the computer to provide online real-time readings of air flow rate.

The variable rate solenoids used for the dissolved oxygen set points 4.0 mg/L to 1.0 mg/L were unable to accurately control the low air flow rates required for the set points below 1.0 mg/L. To obtain accurate control of the low air flow rates it was necessary to use a micrometer based needle valve.

A needle valve was selected that provided a linear response (that is a linear increase in flow rate as the needle valve was opened). As the system had to be automated the needle valve was opened and closed by a stepper motor connected to the process control system. The 8 Bit control system allowed the motor to control the valve by 256 graduations from the closed to the fully open position.

The flow rate from the valve was dependent upon the input pressure but an input pressure of 25 PSI provided for a flow rate from 0 L/min to 9 L/min. The 256 graduations allowed this flow rate to be controlled theoretically in steps of 36 mL/min. The aeration system for the set points below 1.0 mg/L is illustrated in Figure 2.2-2.

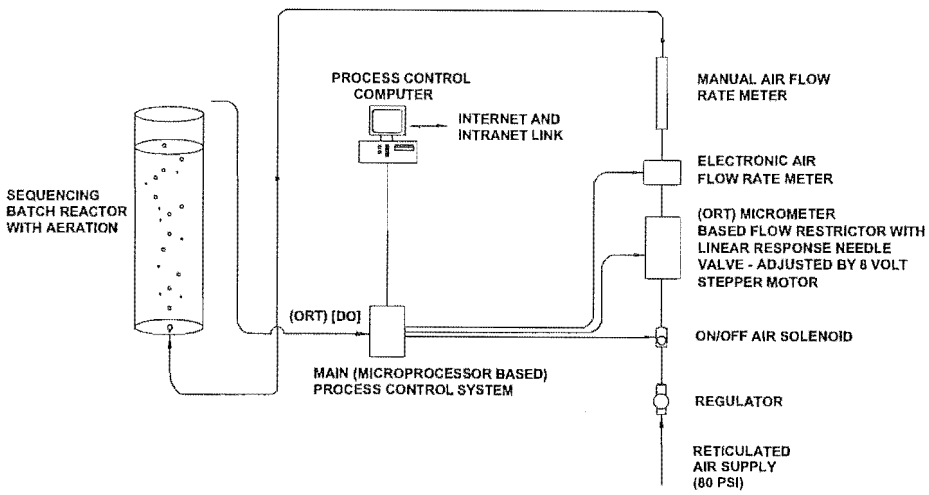


Figure 2.2-2 Aeration system for set points below 1.0 mg/L (Duplicated for second reactor)

Diffusion of oxygen into the reactor was achieved with a single 25 mm diameter sphere-shaped aquarium diffuser. Experimental work (Appendix B3) determined there was little increase in oxygen transfer efficiency when multiple stones or other diffuser types (such as sock diffusers or porous aeration discs) were used. The oxygen transfer efficiency was found to be 3 % (in fresh water at 20 ^{o}C). This compares to values ranging from 27-39 % commonly experienced in full-scale facilities (Metcalf and Eddy (1991)). The main impediment to increasing the transfer efficiency was the depth of the reactor relative to full-scale facilities. Full-scale aeration facilities frequently have depths in excess of 4.5 m while the depth of the lab scale reactor was only 0.38 m. The depth of the aeration tank translates directly into contact time between the diffused air and mixed liquor. As the contact time could not be modified it was necessary to have high air flow rates in order to compensate for the low dissolved oxygen transfer efficiency.

The duration of the aeration phase was determined either by online real time readings or alternatively upon default timer values loaded into the process control system.

Note that low dissolved oxygen concentrations can be maintained by either direct control (as used in this research) or indirect control of the air flow rate. Direct control relies upon readings from online real time dissolved oxygen sensors while indirect control relies upon other process parameters such as ORP or NADH fluorescence. Researchers to use direct control include Osada *et al* (1991) and Suwa *et al* (1992); and use of ORP has been undertaken by Moriyama *et al* (1993) and Collivignarelli and Bertanza (1999); while NADH fluorescence has been used by Helmo (1993).

2.3 PROCESS CONTROL SYSTEM

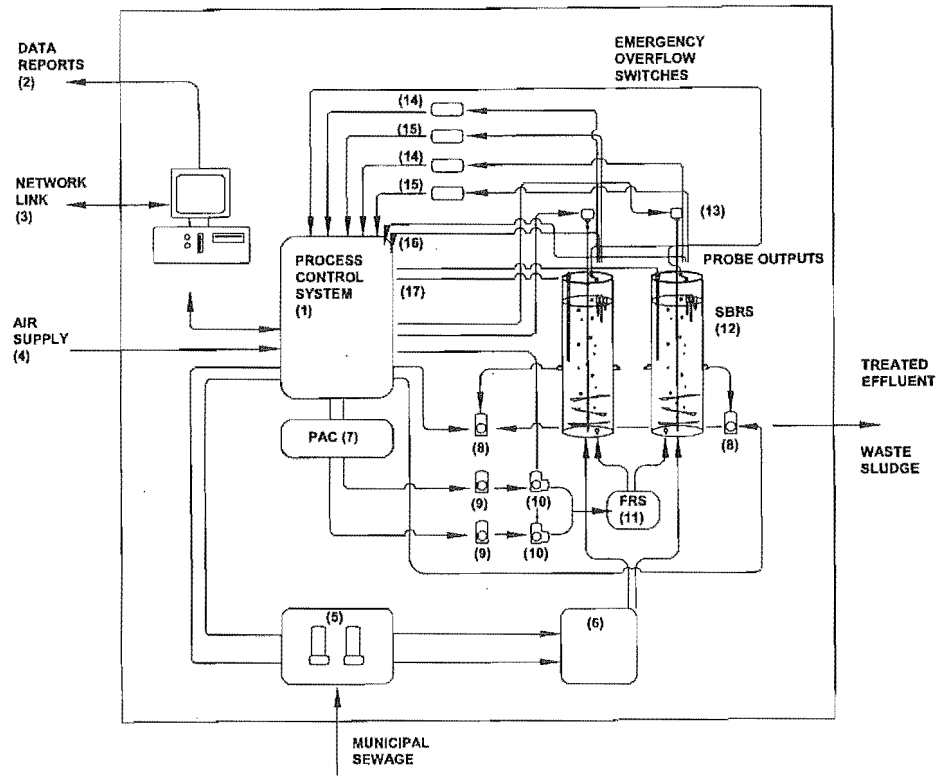
Automated control of the reactors was necessary to allow the experimental setup to run continuously unassisted when no operator was present. A microprocessor

based control system as illustrated in Figure 2.3-1 was developed in house at the University of Canterbury. The process control system was composed of two key elements, a central control box and a personal computer.

The central control box was microprocessor based and contained 16 analogue inputs, 16 digital inputs, and 16 digital outputs. This allowed complete and independent control of all the required reactor operations. Included within the system was an independent "watch dog" microprocessor whose purpose was to maintain control of the reactor on a limited basis in the event of a computer malfunction. The central control box checked the status of the personal computer every six seconds. In the event of identifying a computer problem the watchdog microprocessor was programmed to act as a stand-alone unit operating on a predetermined timer basis until being manually overridden by an operator. This provided additional operational security by reducing the possibility of a "biological" upset, if the computer had problems during an unattended period.

The personal computer ran a software program developed with the Lab View package from National Instruments. The software allowed the computer to control and monitor the process using either an onboard A/D card or via one of the computer communication ports. Other researchers to have used Lab View for this type of application include Yu *et al* (1998) and Andreottola *et al* (2001).

Appendix B1 contains photographs of the experimental hardware including the process control system while Appendix B4 provides a description of the process control software and the algorithms used.



KEY

(1) Process controller, microprocessor control, controlled and monitored on AMD 1 GHz Athlon PC running Windows XP. Box incorporates 16 analogue inputs, 16 digital inputs, and 16 digital outputs.

(2) Online real-time data reports for the analysis of treatment process

(3) Network link allowing for remote access to process control system, for example via intranet and internet.

(4) Regulated compressed air supply

(5) 500Lcapacity cold wastewater storage with submersible feed pumps

(6) Immersion heated water bath

(7) (PAC) Proportional air valve controller

(8) Waste solenoids

(9) Air solenoid

(10) Variable rate air solenoids

(11) (FRS) Electronic flow rate sensors

(12) 8L capacity sequencing batch reactors

(13) Mixers

(14) DO meters

(15) pH meters

(16) ORP cables

(17) Fill control pressure transducers

Figure 2.3-1 Process control system (with attached hardware)*

The process control software displayed and recorded data for ORP, pH, [DO] and airflow (oxygen demand). It was possible to input algorithms to allow the software to interpret the data for process control decisions. For example if the profiles displayed certain features that were correlated to known biochemical events the algorithms could identify these features and then initiate some form of action.

The use of a personal computer allowed some forms of modern communication technology to be incorporated. For example a permanent internet connection permitted remote control and monitoring of the process and provided access to WAP, (Wireless Application Protocol) technology. Access to WAP technology meant that emails or SMS (Short Message Service or txt-text messages) could be sent directly to any (WAP) cell phone allowing the operator to be alerted to conditions while being away from the process. A live Internet based camera was also used to provide remote visual checking of the process performance when the system was unattended. This visual data could also be accessed with any internet connected PC, WAP phone, or pocket PC (with an appropriate display).

As the process control system was developed on the fly, it was periodically necessary to put the reactors under the control of a PLC (programmable logic controller) while maintenance or changes were made to the main system.

2.4 FEED SUPPLY SYSTEM

To store the wastewater and limit degradation, a 500 L chest freezer was purchased and fitted with an external temperature controller built in-house at the University of Canterbury. The temperature controller required the input of a desired temperature set point, it then simply turned the freezer on or off depending upon the actual temperature as measured by a submersed thermostat.

The freezer contained two submersible feed pumps and one submersible mixer pump. The wastewater mixer was connected to a timer which switched the mixer on for 3 minutes of each 15 minute period. This ensured the wastewater composition was as consistent as possible. The mixer pump was located so that mixing could be undertaken without the pump acting as an aerator (thus reducing biological degradation). To prevent the growth and acclimatization of bacteria in the freezer it was emptied and washed thoroughly before each fresh batch of wastewater was added.

By trial and error, it was found that the lowest temperature the wastewater could be safely stored at without risk of forming ice on the sides of the freezer (and possibly damaging the pumps) was 3.8 °C. Since the wastewater temperature at Bromley was typically between 15-20 °C, the large thermal mass of the wastewater (~450 L at 15 °C) meant the freezer typically took 15-20 hours to lower the temperature to the desired 3.8 °C.

The operating temperature of the reactors was approximately 20 °C and since the wastewater was stored at 3.8 °C it was necessary to heat the influent before input into the reactors as low temperatures could slow biological activity. To achieve the required temperature increase, the feed lines from the freezer to the reactors were passed through a water bath (2350 Watt unit produced by Grant Instruments). The polyethylene feed lines were connected to glass heat transfer coils submerged in (potable) water that was heated to approximately 50 °C. The glass coil contact time was a matter of seconds due to the feed line flow velocity. The water bath contained an in-built stirring mechanism which aided the heat transfer. Figure 2.4-1 depicts the water bath used.

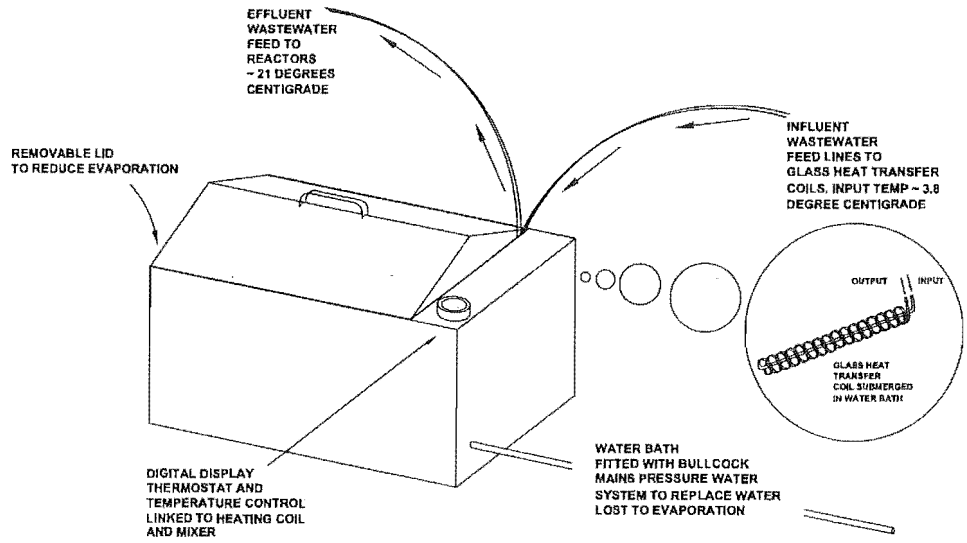


Figure 2.4-1 Heating of wastewater

It is also important to note that the laboratory was air-conditioned to provide a constant air temperature of 20 °C. This resulted in stable/consistent reactor temperatures.

2.5 EXPERIMENTAL OPERATION

The SBR operation had four sequential steps to each cycle namely (1) fill & mix, (2) react (aeration), (3) settle (sedimentation/clarification) and (4) draw (decant). Figure 2.5-1 illustrates the four main steps to each cycle.

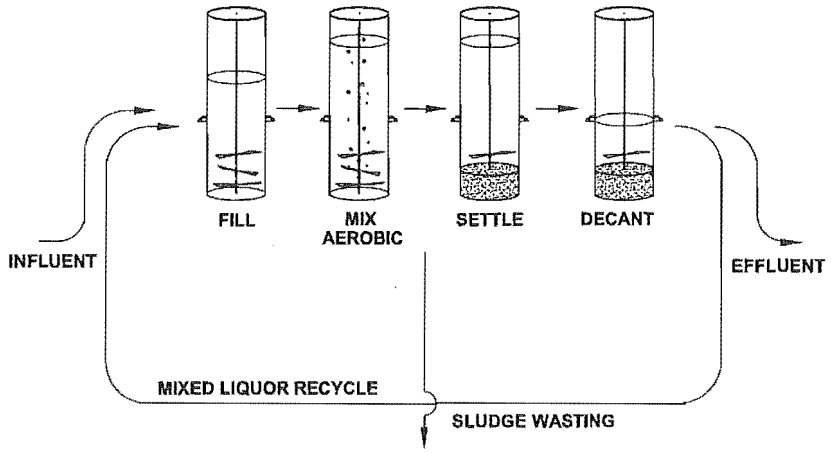


Figure 2.5-1 Representative configuration of the SBR process.

2.6 REACTOR SEED

Activated sludge from the Lyttleton sewage treatment plant, (near Christchurch, New Zealand), was obtained by collecting a 20 L bucket of mixed liquor from the oxidation ditch. The bucket contents were allowed to settle for 30 minutes before the effluent was decanted to provide the seed material (activated sludge). A sample of approximately 200 mL of concentrated sludge (~5000 mg/L) was then used to seed the reactor. Once seeded the reactor was filled to the top with fresh wastewater. To acclimatize and grow the mixed liquor the reactor was initially operated with a default time value of 150 minutes aeration at a DOSP of 4.0 mg/L (instead of online readings).

2.7 REACTOR FEED

The reactor was fed with fresh municipal wastewater obtained from the inflow region of the primary sedimentation tanks at the main Christchurch wastewater treatment plant located at Bromley. Figure 2.7-1 shows a schematic of Bromley wastewater treatment plant with the location of feed collection point.

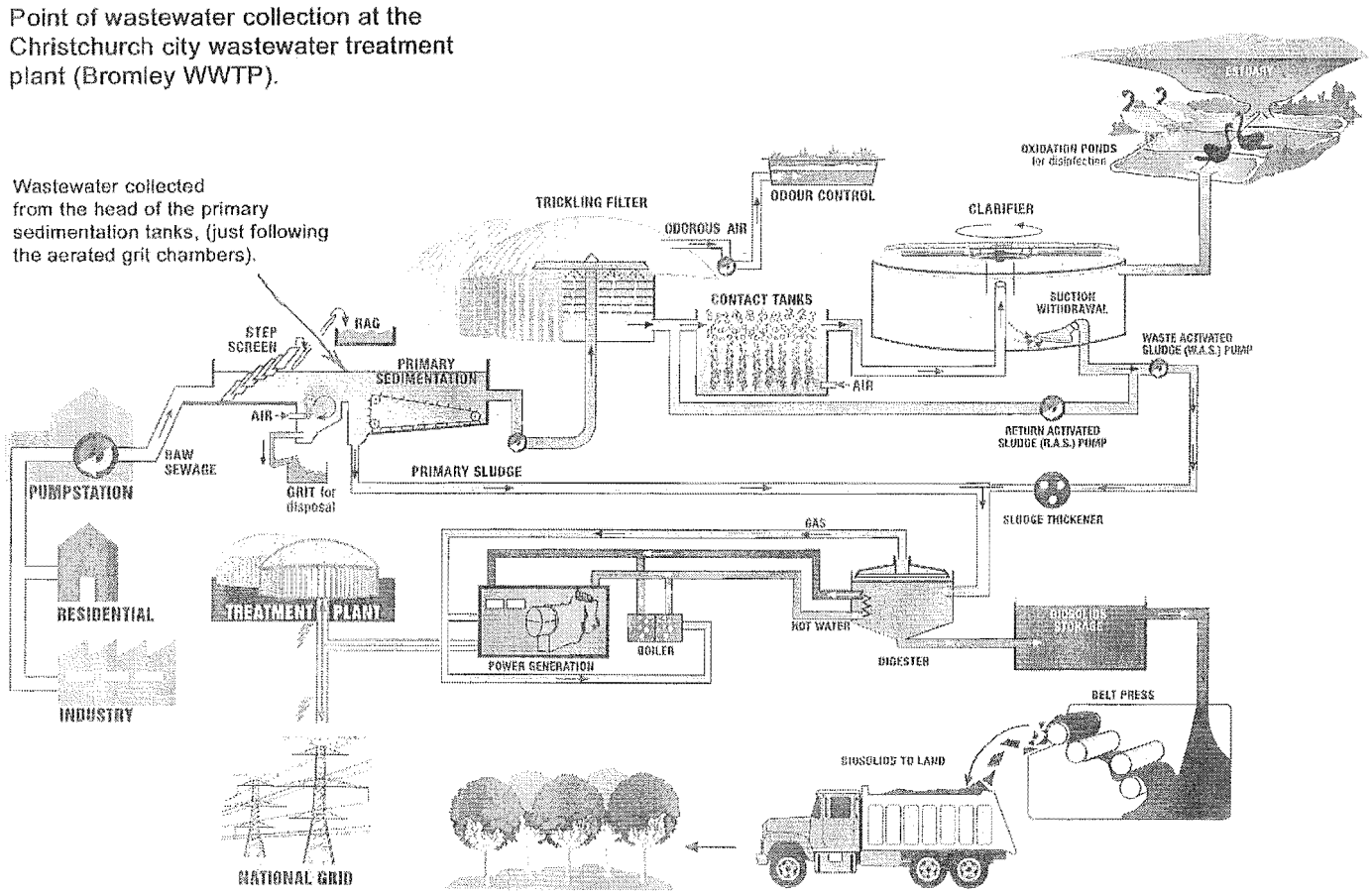


Figure 2.7-1 Schematic of Bromley wastewater treatment plant with the location of experimental feed collection indicated, (Adapted from Christchurch City Council public information brochure).

The wastewater at this point had been through coarse bar screens to remove large objects such as rags and sticks and had been through an aerated grit chamber sequence to remove most of the inert coarse grit. The composition of the wastewater is illustrated in Table 2.7-1 which shows the average values from tests taken over the duration of the work.

Table 2.7-1 Influent wastewater characteristics

	TCOD (mg/L)	SCOD (mg/L)	NH_4 - N (mg/L)	NO_2-N (mg/L)	NO_3-N (mg/L)	TP (mg/L)	TPN (mg/L)	TCOD/TPN
Average	700	350	55	0	0	10	65	11
	total	soluble	total	total	total	total	total	
±σ	91	71	9	0	0	2	9	

The wastewater was obtained once or twice a week depending on requirements. Checks to monitor the wastewater composition while in cold storage were carried out on a regular basis. An example set of tests are presented in Table 2.7-2, these results show the wastewater composition over a seven day period while Figure 2.7-2 illustrates the decline in [COD].

Table 2.7-2 Wastewater degradation while in cold storage

Component mg/L	Mon	Tue	Wed	Thur	Fri	Sat	Sun
COD Unfiltered	674	626	593	544	525	524	496
COD Filtered	380	330	326	280	242	225	191
NH_3-N Filtered	26	33	33	33	33	32	34
NO_2-N Filtered	0	0	0	0	0	0	0
NO_3-N Filtered	0	0	0	0	0	0	0
SS	186	154	157	156	151	145	148

Table 2.7-2 shows the COD declining at an almost linear rate and the ammonia nitrogen increasing slightly as organic nitrogen is converted to the ammonium cation NH_4^+ (wastewater pH was typically between 6.8-7.4). Note the decline in unfiltered COD appears to be largely caused by the fall in soluble COD. The BOD_5/TN ratio for the wastewater was 11 based upon a BOD_5 concentration of domestic wastewater generally around 50% of the unfiltered COD concentration (0.4-0.8 BOD_5/COD Metcalf and Eddy (1991), ~0.5 BOD_5/COD WRC (1984)).

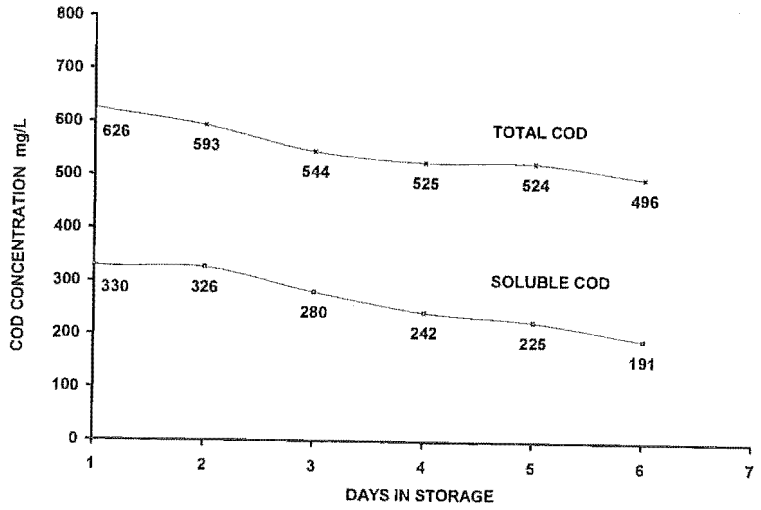


Figure 2.7-2 Organic carbon degradation during wastewater storage

2.8 REACTOR OPERATION AND CONTROL PARAMETERS

The first reaction step involved the introduction of oxygen that was maintained at a specific set point value for the entire aeration phase. This set point was achieved by the variable input of air dependent upon a reading from a dissolved oxygen probe. The actual dissolved oxygen concentration in the reactor relative to the desired concentration determined how much air the control system would supply to the system. The actual air flow rate was measured continuously with an inline electronic air flow meter.

A specific dissolved oxygen concentration was required because it was necessary to investigate biochemical conditions (such as ammonia oxidation rates, nitrite and nitrate reduction rates, development or inhibition of aerobic denitrification) that resulted from operating at specific dissolved oxygen concentrations. With respect to ORP it was necessary to differentiate between ORP changes that resulted from nutrient depletion and those that resulted from changes in the dissolved oxygen concentration. The maintenance of a fixed dissolved oxygen concentration eliminated the possibility of ORP changes resulting from a dissolved oxygen breakpoint.

The duration of the aeration phase was determined by the process control system detecting an online profile feature which had been correlated to the depletion of ammonia nitrogen. There was also a default aeration time which terminated the aeration phase in the event that the online real time control system failed. The default aeration time depended upon the dissolved oxygen set point and the likely time required to oxidize the ammonia nitrogen.

The settle and decant steps were 15 and 5 minutes respectively and were controlled by a timer within the process control system. The fill step was dependent upon a fill level sensor; however this phase typically lasted 2-3 minutes.

The quantity of the clarified effluent that was decanted at the end of each cycle was set at 50 % of the reactor volume or approximately 4.0 L (Total used reactor volume 8.0 L). Sludge wasting was undertaken manually during the fully mixed aeration cycle. It was not included as one of the main process steps as there was no set time period within each cycle dedicated to wasting. No wasting was undertaken during a track study.

The amount and frequency of sludge wasting was determined by taking regular [MLSS] readings with the objective being to maintain the reactor within +/- 10% of the desired operational [MLSS] of 3000 mg/L, (i.e. 2700-3300 mg/L). The desired operational [MLSS] of 3000 mg/L was chosen following classification of the wastewater as medium-high strength. With reference to Table 2.7-2 the wastewater total COD while in cold storage was typically between 500-650 mg/L, this corresponds to a medium-high strength wastewater. Typical design parameters for sequencing batch reactors detailed in MetCalf and Eddy (2001) give an operational MLSS range of 2000-5000 mg/L dependent upon factors such as the COD concentration. The SRT was an independent parameter that changed depending upon the relative growth rates of the bacteria.

2.9 REACTOR COMISSIONING

The reactors were run for nearly 18 months. The first 7 months were used for development of the hardware. Following the developmental phase the reactors were seeded and operated for six months before the official runs were undertaken, during this time the reactors were operated at a range of dissolved oxygen concentrations between 0.5 - 5.0 mg/L. The first run was initiated subsequent to this six-month period using the acclimatized reactor biomass. The reactors were operated continuously from the point of initial seeding to the point of decommissioning.

There were no replicate runs undertaken in an attempt to duplicate the results, this was largely due to time constraints. The experimental work experienced considerable delays due to difficulties experienced during the research. Difficulties included software bugs, hardware problems, and solving electrical problems (particularly ground loops).

Chapter 3 EXPERIMENTAL TESTING

3.1 TESTING UNDERTAKEN

Table 3.1-1 illustrates the parameters that were monitored during the experimental work.

Table 3.1-1 Chemical parameters monitored

Chemical parameters monitored	
Total nitrogen	TN
Ammonia nitrogen	NH_3-N
Nitrite nitrogen	NO_2-N
Nitrate nitrogen	NO_3-N
Total phosphorus	TP *
Ortho phosphorus	Ortho-P *
Chemical Oxygen Demand	COD
Suspended Solids	SS
(On-line) Oxi-Red potential	ORP
(On-line) Hydrogen ion concentration	pH
(On-line) Dissolved Oxygen	DO

* Measured in the influent wastewater only

All samples were taken while the reactor contents were fully mixed and were vacuum filtered through Whatman glass fiber filters (GF/C) (grade C particle retention 1.2 um) followed by Millipore griddled membrane filters made from mixed esters of cellulose optimized for microbiological analysis of water (type HA 0.45 um). Retained activated sludge from the filtering process was returned to the reactor. Certificates of quality for the filters used confirm Standard Methods compliance. With the exception of MLSS and the on-line parameters, samples were analyzed using HACH Test 'N Tube products. Readings were taken on a HACH DR/2000 spectrophotometer as it provided consistently accurate results. Table 3.1-2 provides a description of the analysis methods used.

Table 3.1-2 Chemical parameters analyzed using colorimetric methods

Parameters tested with HACH Test 'N Tube products	Method Number	Method Description	Range	Designed for testing
Total phosphorus	8190	PhosVer3 with acid persulfate digestion	0-3.5 mg/L	Water - wastewater - sea water
Orthophosphate (reactive)	8048	Ascorbic acid method	0-2.5 mg/L	Water - wastewater - sea water
Oxygen demand COD	8000	Colormetric measurement	0-1500 mg/L COD	Water - wastewater - sea water
Total nitrogen TPN	10071	Persulfate digestion method	0-25 mg/L N	Water - wastewater
Ammonia	10031	HR Salicylate method	0-50 mg/L NH_3-N	Water - wastewater - sea water
Nitrite	8153	HR Ferrous sulfate method	0-150 mg/L NO_2^- (0-45 mg/L NO_2-N)	Water - wastewater
Nitrate	8039	HR Cadmium reduction method	0-30 mg/L NO_3-N	Water - wastewater - sea water

*HR = High Range version of the test

* When sample concentrations exceeded the test range they were diluted with demineralised water

The filtered sample sizes required for analysis on the DR/2000 varied between 0.2 - 25 mL. For a complete analysis of COD, TN, NH_3-N, NO_2-N, and NO_3-N an initial sample size of approximately 70 mL would be withdrawn from the reactor which would then be filtered before sub-samples for the various chemical parameters were taken. Experimental work was usually limited to specific testing runs where a single cycle would be intensively analyzed during a track study, i.e. samples would usually be taken every 10 - 15 minutes with the main emphasis upon COD and the various forms of nitrogen.

The test for TN involved the use of a HACH alkaline persulfate digestion method known as TPN. The Total Persulfate Nitrogen (TPN) measurement is a test offered by HACH that provides a measure of nitrogen similar to the traditional Total Kjeldahl Nitrogen (TKN) test except the procedure is faster and eliminates hazardous Kjeldahl-method materials. The HACH method is based upon the procedure in Standard Methods for the Examination of Water and Wastewater 20th Edition Method 4500-P E., p. 4-146. An evaluation of the TPN method was undertaken by Langner and Hendrix (1982).

The TPN test is finding application in the monitoring of total nitrogen within wastewater treatment facilities. The TPN test uses an alkaline persulfate digestion to convert all nitrogen forms to nitrate nitrogen. The nitrate reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum at 410 nm, measurement of the yellow complex is undertaken on a spectrophotometer. The test measures all forms of nitrogen such as soluble forms of ammonia, nitrate and nitrite as well as soluble and insoluble forms of organic nitrogen (BIOLAB Scientific (2003) Product technical information). Table 3.1-3 provides an illustration of the types of nitrogen measured in both the TPN and other nitrogen tests used in this research.

Table 3.1-3 HACH nitrogen tests used in this research

	Organic nitrogen	Ammonia	Nitrite	Nitrate
TPN Test 'N Tube				
Ammonia Test 'N Tube				
Nitrite Test 'N Tube				
Nitrate Test 'N Tube				

While the TPN test measured insoluble forms of nitrogen all samples in this research were filtered to the 0.45 um level making it unlikely that insoluble particulate matter was present in significant quantities.

Sampling for [MLSS] was undertaken on a daily basis. Sample sizes were between 90 -100 mL; these were vacuum filtered through a Whatman glass fiber filter (GF/C) (grade C particle retention 1.2 um) that had been oven dried at 110 ^{o}C for 24 hours prior to the test. The filtered samples were then dried at 110 ^{o}C for 24 hours and the MLSS was determined by calculating the retained/filtered solids following standard methods 208 D.

3.2 SAMPLE PRESERVATION AND STORAGE

Samples were collected in clean plastic or glass bottles. The bottles for phosphorus samples were acid cleaned with 1:1 hydrochloric acid solution and rinsed with demineralised water. Detergents containing phosphate were avoided when cleaning sample bottles used in the tests.

All samples taken from the reactor were tested immediately. Some samples of wastewater from Bromley wastewater treatment plant and from the feed cooler were unable to be tested shortly after sampling and were preserved prior to storage. The preservation was necessary to prevent degradation of the sampled material and loss of test accuracy. Samples preserved by adding liquids had to have adjustments made to their final test results to allow for the dilution effects/volume changes of the original sample. It should be noted that preservation was rarely undertaken due to the possible detrimental effects on result accuracy and complications involved in preserving small sample sizes.

Duplicate analyses were undertaken on a "casual basis" to ensure confidence in the results. A statistical analysis of the duplicate tests was not undertaken. The following storage and preservation methods were used.

3.2.1 COD

For sample storage periods up to 28 days, sulfuric acid was added to the filtered sample until the pH was less than 2.0. The sample was then placed in cold storage at 4 ^{o}C or below. Immediately prior to analysis the preserved sample was warmed to room temperature.

3.2.2 TPN

Preservation involved reducing the pH to 2 or less with concentrated sulfuric acid. The samples were then stored at 4 ^{o}C or less for up to 28 days. Immediately prior to analysis the samples were warmed to room temperature and the pH was neutralized with 5 N sodium hydroxide.

3.2.3 NH_3-N

The sample was preserved for up to 28 days by reducing the pH to 2 or less and refrigerating at 4 °C or less. Immediately prior to analysis the sample was warmed to room temperature and the pH was neutralized with 5 N sodium hydroxide.

3.2.4 NO_3-N

Samples could be preserved at 4 °C or lower, providing they were analyzed within 48 hours. Prior to testing, the samples were warmed to room temperature. For longer storage periods, the pH was adjusted to 2 or less with sulfuric acid and the sample was refrigerated. Before testing the preserved sample was warmed to room temperature and the pH was neutralized with 5.0 N sodium hydroxide standard solution.

3.2.5 NO_2-N, ORTHO P, AND TP

If samples were to be analyzed within 48 hours (24 hours for TP) then cold storage at 4 °C or lower was satisfactory. For longer storage periods mercuric chloride solution was added in the ratio of 4.0 mL/1000 mL of sample however sample refrigeration was still required. Both methods required the samples to be warmed to room temperature before any test work was undertaken. The samples preserved with mercuric chloride had to have a sodium chloride level of 50 mg/L or higher to prevent mercury interference in the test; samples low in chloride could be spiked with approximately 1 mg sodium chloride.

3.3 ON-LINE MONITORING

On-line monitoring of ORP, pH, and [DO] was undertaken continuously with each reactor having its own associated electrodes/probes "permanently" fitted. Results were logged automatically on a dedicated data-logging PC. A real time plot was also automatically produced on the logging PC allowing monitoring of biological activity to be undertaken while a cycle was in progress. Readings for calculation

purposes were taken every six seconds while for plotting purposes every sixty seconds.

3.3.1 ORP

Platinum band electrodes were used as described in the literature review. The ORP electrodes were connected directly to the process control system. The ORP probes were cleaned frequently (which involved wiping with a damp sponge). Failure to regularly clean ORP probes can result in the variation rate and the variation range of the ORP reading being affected (Paul *et al* (1998), Collivignarelli and Bertanza (1999)). The probes were also periodically checked in quinhydrone buffer solution following the method specified by BIOLAB Scientific (2003) Product technical information.

3.3.2 pH

The pH was measured on EDT (RH357Tx) microprocessor controlled meters fitted with "field grade" glass body electrodes; both meters provided a mV output which was fed to the data logging PC.

Both the pH and the dissolved oxygen meters had the ability to measure the temperature within the reactors. This was checked periodically to ensure the water bath was working correctly.

3.3.3 DO

The presence and concentration of dissolved oxygen within the reactors was measured using YSI Model 57 dissolved oxygen meters (one for each reactor). The probes used membrane-covered clark-type polaragraphic sensors which were covered with a thin permeable membrane. High sensitivity membranes (half the thickness) were used to allow accurate readings at low DO concentration levels. The meters provided a mV output which was fed to the process control system.

Chapter 4 EXPERIMENTAL RESULTS SUMMARY

4.1 INTRODUCTION TO EXPERIMENTAL RESULTS

The following section provides a summary of the results. A full set of results including plots for operational variables such as [MLSS] and SRT are presented in Appendices A1 to A4.

The investigation of aerobic denitrification was undertaken in a series of periods called runs, each run represented the operation of the reactors at a different dissolved oxygen concentration. The following aspects should be noted before review of the runs.

1) One operational objective was to maintain the mixed liquor suspended solids concentration at 3000 mg/L +/- 10 % (i.e. 2700-3300 mg/L). It was not possible to maintain a target SRT as it was dependant upon the growth rate of the biomass. The slower biomass growth rates at lower dissolved oxygen concentrations resulted in a considerable increase in SRT. The effect of DO concentration on SRT can be illustrated in Figure 4.1-1 which shows the SRT required to achieve an effluent ammonia concentration less than 1.0 mg/L (at 20°C) in a completely mixed activated sludge system (adapted from Metcalf and Eddy (2001)).

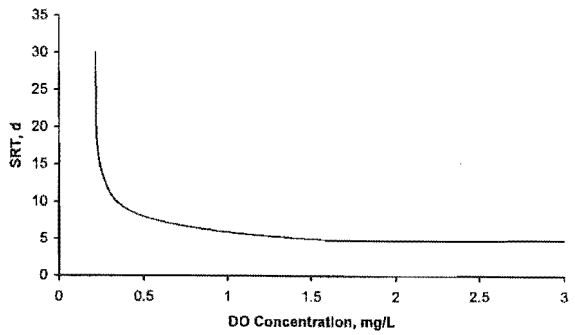


Figure 4.1-1 Effect of DO concentration on SRT required to achieve effluent ammonia concentrations less than 1.0 mg/L in a completely mixed activated sludge system (adapted from Metcalf and Eddy (2001)).

2) The SRT profiles for the set points 1.0 mg/L and 0.5 mg/L (Figures 4.4-3 and 4.5-3) displayed almost a cyclic pattern. This pattern was the result of the low MLSS growth rates and the effects of the wasting regime. The amount of biomass wasted each event was kept similar to the previous runs however the low dissolved oxygen concentration meant it took the system allot longer to recover. The greater period between wasting events resulted in a significant impact on the calculated SRT value and the production of a cyclic (saw toothed) pattern on the SRT profile.

3) The wastewater temperature at Bromley was typically between 15-20 °C. When a new load of feed was obtained the large thermal mass of the wastewater (~450 L at 15 °C) meant the storage freezer typically took 15-20 hours to lower the temperature to the desired 3.8 °C. The implication of a higher wastewater temperature during this period was that the influent temperature to the reactor was also slightly higher (~24 °C as a result of the water bath). It was noted that slightly higher MLSS growth rates following the delivery of fresh wastewater were sometimes experienced. It was thought that these higher growth rates may have been linked to the warmer reactor temperatures during this period (a 10 °C increase in temperature can result in doubling of metabolic and growth rates (Metcalf and Eddy (1991)).

4) The settleability of the sludge was excellent throughout the entire period of operation with the sludge volume index between 50 -100 mL/g resulting in a low effluent suspended solids content, (typically less than 5 mg/L following a 15 minute settle period).

5) During each run an intensive chemical parameter testing program (a series of track studies) was undertaken along with on-line monitoring of ORP, pH, DO and air demand to provide real-time analysis of conditions.

The track studies included samples for TN, NH_3-N, NO_2-N, NO_3-N, and COD, which were taken periodically through out a cycle. The chemical results were then plotted against the online profiles for each run in which the operational dissolved oxygen concentration was the variable. All the track study results are primarily limited to the aeration phase of a treatment cycle.

6) The nitrogen loss calculations in this study were based upon the change in [NH_3-N], the possible nitrogen assimilated, the change in [NO_2-N] and the change in [NO_3-N]. Organic nitrogen was not included. Measurements for TPN (which includes organic nitrogen) were undertaken but only to provide a check/confirmation of the nitrogen mass balance calculations. An example calculation for the estimated assimilation is provided in appendix A1.1.

7) Nitrogen mass balance calculations required an estimate of assimilated nitrogen to be undertaken. A literature review indicated that others operating similar lab-scale batch reactors incorporating aerobic denitrification have not incorporated nitrogen assimilation within their nitrogen loss calculations (Munch *et al* (1996), Helmer and Kunst (1998), Pochana and Keller (1999)). This is most probably because the nitrogen loss to assimilation is considered small compared to that lost to biological oxidation-reduction reactions. Research by Patureau *et al* (1998) found that the amount of nitrogen lost to assimilation in a nitrifying sequencing batch reactor was around 1%. Assimilation calculations in this research were based upon the change in the volatile mixed liquor suspended solids concentration and estimates of the likely nitrogen component of the new cell material produced.

8) Inaccuracies in measurement of the MLSS concentration have contributed to inaccuracies in the assimilation estimates. A series of MLSS concentration measurements revealed the test was only accurate to ~ 200mg/L.

9) This research did not take into account the ammonium nitrogen produced from organically bound nitrogen.

10) Depletion of the COD refers to the depletion of readily biodegradable COD. While the COD results sometimes suggest the presence of oxidisable products beyond the point of "COD depletion" these products can most probably not be readily oxidised by the biomass. Thayalakumaran *et al* (2003) also experienced a similar residual effluent soluble COD. They operated a lab scale SBR in a nitrogen removal mode treating meat processing effluent. They defined the residual COD as "soluble non-biodegradable" as reflected by no further soluble COD reduction following prolonged aeration in their system.

11) With reference to the analysis of the pH profiles the pH scale had a 0.8 unit difference for the 4.0 mg/L and 2.5 mg/L DO set points. However the 1.0 mg/L and 0.5 mg/L set points have a 0.4 unit difference. This should be noted before comparing plots from different runs. Prior to the discussion of results examples of one track study from each operational dissolved oxygen set point follow. For a full set of results refer to the appendices.

12) While the ORP, pH, and airflow profiles were all evaluated for their potential use as process control tools only the pH profile was eventually used, that is an algorithm was developed and demonstrated to detect the point of ammonia depletion on the pH profile (ammonia valley).

Chapters 4.2 – 4.5 provide a summary of the specific dissolved oxygen set points. The "finer nuances" of the results are presented in Table 4.1-1.

Table 4.1-1 Summary of results DOSP 4.0 mg/L – 0.5 mg/L

DOSP (mg/L)	% TN assimilated	% initial TN loss unaccounted (mg/L)	Ave [MLSS] (mg/L)	[MLSS] (mg/L) ± σ	Ave cycle time (mins)	Cycle time ± σ (mins)	Ave SRT (days)	SRT (days) ± σ	Ave final NO_2-N (mg/L)	Aerobic denitrification
4.0	14	7	3101	376	153	18	9	1	1	NO
2.5	12	12	2985	490	175	26	8	1	1	NO
1.0	11	28	3165	322	283	16	15*	2	5	YES
0.5	11	40	3024	296	445	20	29.3*	3	10	YES

* The SRT for the aerobic denitrification process in this research ranged between 15-29 days, this corresponds to values of 15-25 days reported by Munch *et al* (1996) .

4.2 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 4.0 mg/L

The reactor was operated at a dissolved oxygen set point of 4.0 mg/L and allowed to run for an acclimatization period of 14 days. Since the SRT for this run was approximately 9 days this period was slightly less than two sludge ages. Seven track studies were undertaken at dissolved oxygen set point 4.0 mg/L, the track studies were undertaken over a one-month period following the 14-day acclimatization period. The online profiles were consistent within 2-3 days (their stability suggesting acclimatization of the system). This section provides a summary and example of the results while Appendix A1 contains a full set of results. Figure 4.2-1 shows the [MLSS] over the duration of the run.

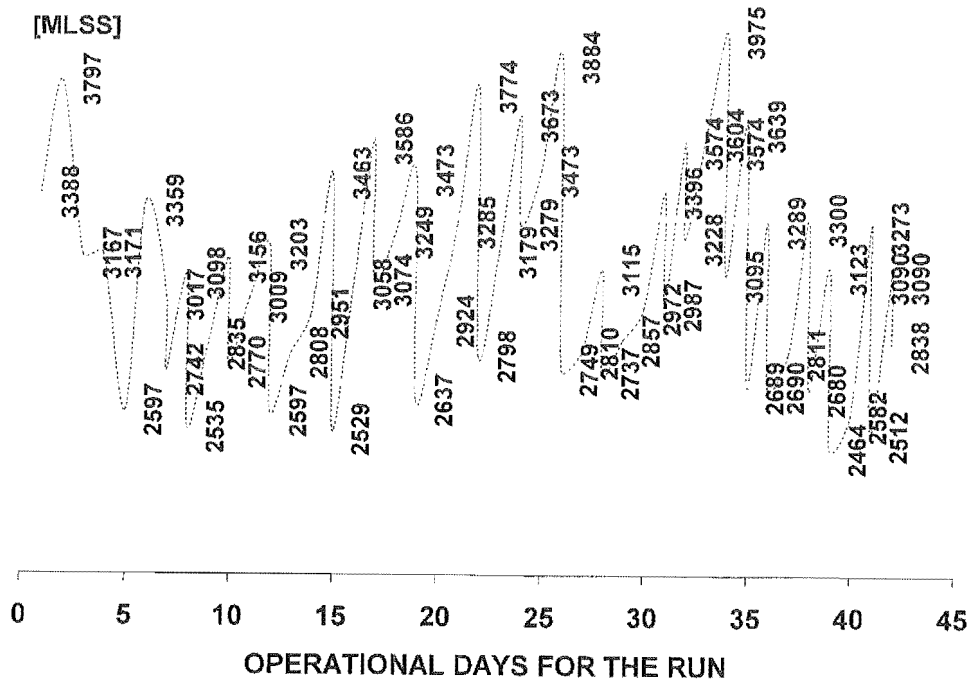


Figure 4.2-1 Mixed liquor suspended solids concentration DOSP 4.0 mg/L

The wasting rate required to keep the [MLSS] close to 3000 mg/L is illustrated in Figure 4.2-2, while Figure 4.2-3 shows the SRT of the system.

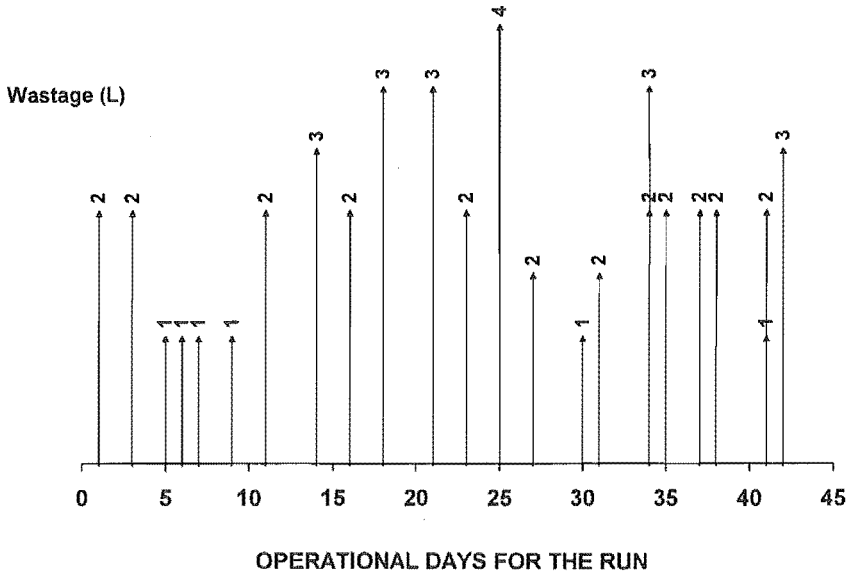


Figure 4.2-2 Mixed liquor wastage DOSP 4.0 mg/L

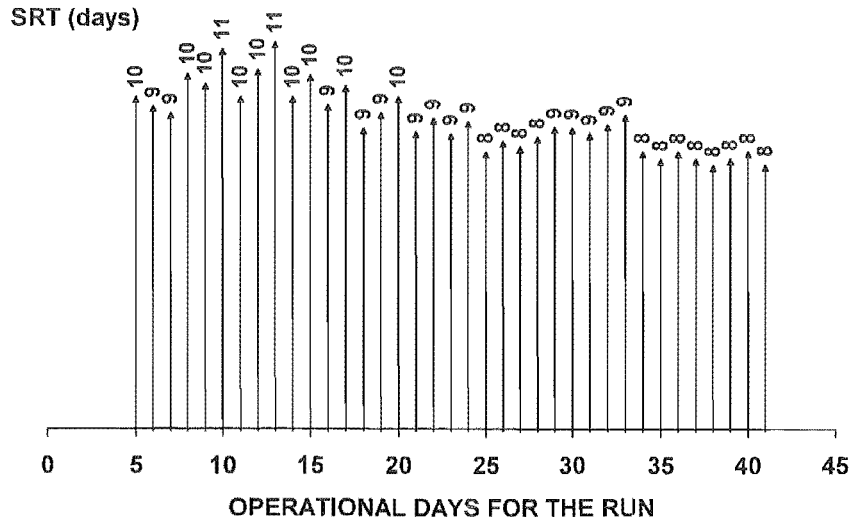


Figure 4.2-3 Solids residence time DOSP 4.0 mg/L

Table 4.2-1 provides a summary of the seven track studies undertaken at DOSP 4.0 mg/L while Table 4.2-2 shows the average values corresponding to the hydraulic residence time.

Table 4.2-1 Summary of track study data [operational dissolved oxygen] 4.0 mg/L

Parameter		Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave	
[MLSS]		mg/L	3300	3586	3115	3074	2972	3639	3179	3266	
Initial NH_3-N		mg/L	20	22	20	19	21	20	19	20	*
Final NH_3-N		mg/L	0	0	0	0	0	0	0	0	
Del NH_3-N	(A)	mg/L	20	22	20	19	21	20	19	20	
Initial NO_2-N		mg/L NO_2-N	0	2	1	0	1	1	0	1	*
Final NO_2-N		mg/L NO_2-N	1	1	0	1	0	1	1	1	
Del NO_2-N	(B)	mg/L NO_2-N	1	-1	-1	1	-1	0	1	0	
Initial NO_3-N		mg/L NO_3-N	4	5	5	6	6	5	8	6	*
Final NO_3-N		mg/L NO_3-N	16	23	20	20	24	18	21	20	
Del NO_3-N	(C)	mg/L NO_3-N	12	18	15	13	17	13	13	15	
Nitrogen loss	(D) = (A - (B+C))	mg/L N	7	5	7	5	4	7	5	6	
Estimated assimilated nitrogen	(E)	mg/L N	5	5	4	2	1	6	4	4	
Unaccounted for nitrogen loss	(F) = (D-E)	mg/L N	2	0	3	3	3	1	1	2	
Nitrification rate		mg/L.min N	0.17	0.21	0.14	0.18	0.16	0.14	0.19	0.17	
		mg/L.min.mg MLSS	5.E-05	6.E-05	4.E-05	6.E-05	6.E-05	4.E-05	6.E-05	5.E-05	
Rate unaccounted N loss		mg/L.min N	2.E-02	0.E+00	2.E-02	3.E-02	2.E-02	6.E-03	9.E-03	1.E-02	
% Initial TN removal		%	29	17	25	19	15	27	17	21	
% TN assimilated		%	21	17	15	7	4	24	14	14	**
% Initial TN loss unaccounted		%	9	0	10	12	11	3	3	7	***
TPN Initial	(G)	mg/L N	27	31	29	29	30	29	30	29	
TPN Final	(H)	mg/L N	19	25	22	24	26	22	25	23	
TPN loss	(I) = (G-H)	mg/L N	8	5	7	5	4	7	5	6	
COD Initial	(J)	mg/L N	125	175	161	145	159	152	161	154	
COD Final	(K)	mg/L N	19	24	23	22	21	22	20	22	
COD loss	(L)=(J-K)	mg/L N	106	151	138	123	138	130	141	132	

Table 4.2-2 Summary of HRT values DOSP 4.0 mg/L

Parameter	Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave
Cycle time	minutes	148	134	187	143	147	165	146	153
HRT	days	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2
Cycle/day	Cycle/day	9.7	10.7	7.7	10.1	9.8	8.7	9.9	10

With reference to Table 4.2-1 the average influent soluble nitrogen (TN) was 27 mg/L (not including soluble organic N, this figure composed of 20 mg/L NH_3-N, 1 mg/L NO_2-N, and 6 mg/L NO_3-N, refer * Table 4.2-1). Fourteen percent of the influent soluble nitrogen was assimilated into new cell tissue; the remainder was mostly transformed to NO_x-N (refer ** Table 4.2-1).

Seven percent (refer *** Table 4.2-1) of the initial total nitrogen could not be accounted for in the nitrogen mass balance procedure.

The main cause of error came from the calculations regarding assimilation; these required the measurement of [MLSS] at the start and end of the cycle. The difference in the two readings was then taken to calculate the nitrogen assimilation. A series of tests on mixed liquor (MLSS concentration 3000 mg/L) showed that two tests on the same material had a difference of up to 200 mg/L. The actual change in [MLSS] over the length of a cycle was usually 20-40 mg/L, thus an accurate determination of assimilation was not possible. See discussion 5.1, it is possible the assimilation calculations also over estimated the amount of nitrogen assimilated into new cell material.

It is unlikely that the unaccounted for nitrogen can be attributed to aerobic denitrification due to the high dissolved oxygen concentration. The pH of the reactor was also too low (~6.8-7.8) for air stripping to be a pathway for ammonia loss.

The online real time plots for pH and air flow provided some useful features that could be correlated to biochemical events. Figure 4.2-4 shows a typical pH profile with the ammonia valley (point 1) indicating the point of ammonia depletion, (all profiles taken from TS1 DOSP 4.0 mg/L).

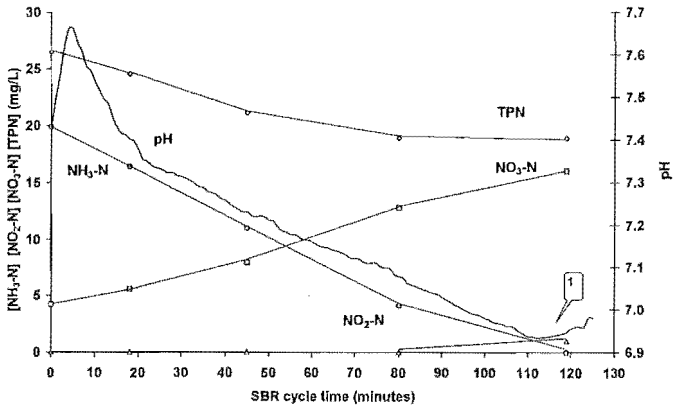


Figure 4.2-4 pH and [soluble nitrogen]

The pH curves provided profiles with consistently clear features. The ammonia valley, (as described in section 1.6), was so distinguishable and consistent that an algorithm was developed so that the process control system could use the feature to determine the point of ammonia depletion. The process control system detected the point of ammonia depletion using the pH algorithm in 419/420 cycles giving a successful detection rate equal to 99.8% reliability. Figure 4.2-5 shows the air flow profile with ammonia and COD data.

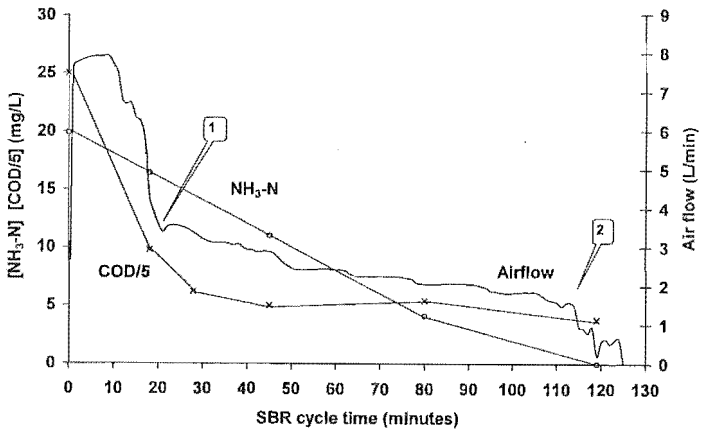


Figure 4.2-5 Air flow rate [NH_3-N] and [COD]

The depletion of COD was indicated by a transition to a somewhat level gradient on the air flow profile (point 1 Figure 4.2-5) while the depletion of ammonia

appeared as a drop in the air demand at the end of the cycle (point 2 Figure 4.2-5). A visual inspection of the 420 profiles resulted in an estimate that the air flow profile could have been used for determination of the point of COD and ammonia depletion in 80% and 40% of the cycles respectively. The ammonia depletion feature was inconsistent in that the feature was often not distinct and the shape of the feature did not lend itself to be reliably detected by an algorithm. The 40% detection rate would suggest the ammonia depletion feature is unlikely to provide a reliable process control tool however it could be used for manual interpretation by an experienced operator. No algorithms were developed in this research to provide automated process control from the air flow profile. Figure 4.2-6 shows the ORP and dissolved oxygen profiles.

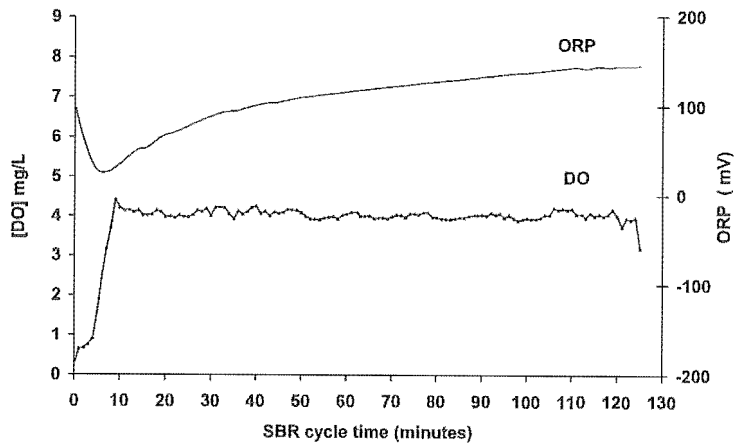


Figure 4.2-6 ORP and [DO]

The ORP profile did not show any distinguishing features that would enable it to be used as a process control tool. The operation at a fixed dissolved oxygen concentration meant that changes to ORP could only result from changes in oxidation reduction potential resulting from nutrient depletion rather than by changes in dissolved oxygen concentration (i.e. the ORP profile did not change due to factors such as DO breakthrough).

4.3 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 2.5 mg/L

The reactor was set to a dissolved oxygen set point of 2.5 mg/L and allowed to run for an acclimatization period of 19 days. Since the SRT for this run was approximately 8 days this period was slightly greater than two sludge ages. As with the previous DOSP consistent behavior (in terms of online profiles) was established well before the end of the acclimatization period. Seven track studies were undertaken at dissolved oxygen set point 2.5 mg/L. The track studies were obtained over a one-month period following the 19-day acclimatization period. This section provides a summary and example of the results while Appendix A2 contains a full set of results. Figure 4.3-1 shows the [MLSS] over the duration of the run.

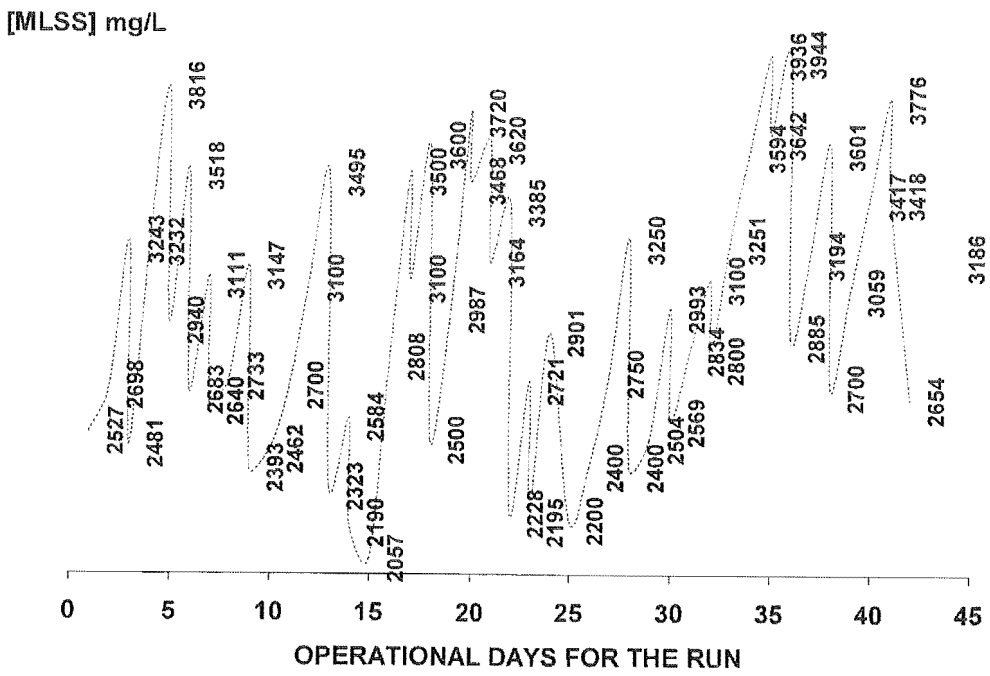


Figure 4.3-1 Mixed liquor suspended solids concentration DOSP 2.5 mg/L

The wasting rate required to keep the [MLSS] close to 3000 mg/L is illustrated in Figure 4.3-2 while Figure 4.3-3 shows the SRT of the system.

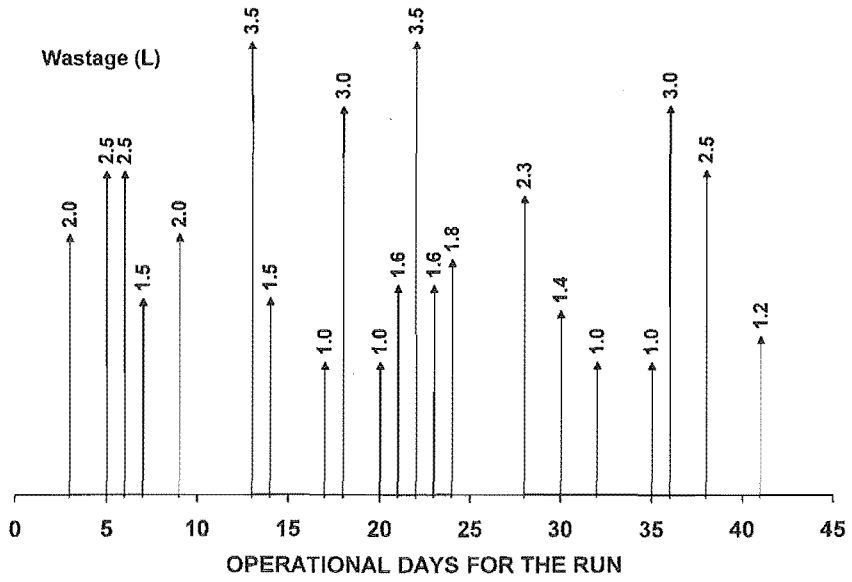


Figure 4.3-2 Mixed liquor wastage DOSP 2.5 mg/L

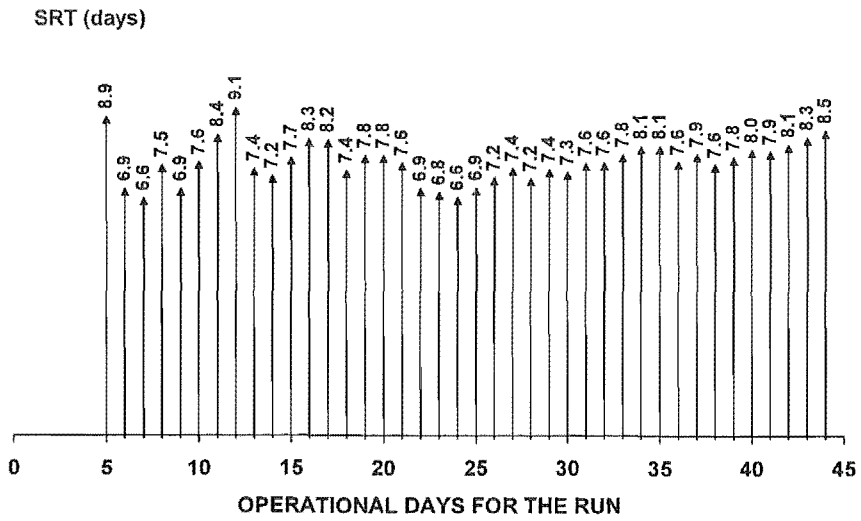


Figure 4.3-3 Solids residence time DOSP 2.5 mg/L

Table 4.3-1 provides a summary of the seven track studies undertaken at DOSP 2.5 mg/L while Table 4.3-2 shows the average values corresponding to the hydraulic residence time.

Table 4.3-1 Summary of track study data [operational dissolved oxygen] 2.5 mg/L

Parameter		Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave	
[MLSS]		mg/L	2504	2901	3620	3944	2834	3194	3594	3227	
Initial NH_3-N		mg/L	19	21	20	18	19	16	20	19	*
Final NH_3-N		mg/L	0	1	2	0	0	1	1	1	
Del NH_3-N	(A)	mg/L	18	20	17	18	18	15	19	18	
Initial NO_2-N		mg/L NO_2-N	2	1	0	0	0	1	0	1	*
Final NO_2-N		mg/L NO_2-N	1	1	1	0	1	1	0	1	
Del NO_2-N	(B)	mg/L NO_2-N	-1	0	1	0	1	0	0	0	
Initial NO_3-N		mg/L NO_3-N	5	6	5	2	6	4	4	4	*
Final NO_3-N		mg/L NO_3-N	20	18	18	16	17	12	15	17	
Del NO_3-N	(C)	mg/L NO_3-N	15	13	13	14	12	8	11	12	
Nitrogen loss	(D) = (A - (B+C))	mg/L N	5	8	3	4	6	7	8	6	
Estimated assmilated nitrogen	(E)	mg/L N	1	3	2	3	3	3	5	3	
Unaccounted for nitrogen loss	(F) = (D-E)	mg/L N	3	5	1	1	3	4	3	3	
Nitrification rate		mg/L.min N	0.12	0.12	0.13	0.16	0.14	0.14	0.11	0.13	
		mg/L.min.mg MLSS	5.E-05	4.E-05	4.E-05	4.E-05	5.E-05	4.E-05	3.E-05	4.E-05	
Rate unaccounted N loss		mg/L.min N	2.E-02	3.E-02	1.E-02	3.E-03	2.E-02	3.E-02	2.E-02	2.E-02	
% Initial TN removal		%	18	27	13	22	24	34	34	25	
% TN assimilated		%	5	10	8	15	11	16	20	12	**
% Initial TN loss unaccounted		%	13	17	5	7	12	18	14	12	***
TPN Initial	(G)	mg/L N	29	31	28	23	27	23	27	27	
TPN Final	(H)	mg/L N	24	23	25	19	21	16	19	21	
TPN loss	(I) = (G-H)	mg/L N	5	8	3	4	6	7	8	6	
COD Initial	(J)	mg/L N	149	180	147	121	128	115	170	144	
COD Final	(K)	mg/L N	19	19	28	12	19	22	19	20	
COD loss	(L)=(J-K)	mg/L N	130	161	119	109	109	93	151	125	

Table 4.3-2 Summary of HRT values DOSP 2.5 mg/L

Parameter	Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave
Cycle time	minutes	170	207	191	145	152	153	206	175
HRT	days	0.2	0.3	0.3	0.2	0.2	0.2	0.3	0.2
Cycle/day	Cycle/day	8.5	7.0	7.5	9.9	9.5	9.4	7.0	8.4

With reference to Table 4.3-1 the average influent soluble nitrogen (TN) was 24 mg/L (not including soluble organic N, this figure composed of 19 mg/L NH_3-N, 1 mg/L NO_2-N, and 4 mg/L NO_3-N, refer * Table 4.3-1). Twelve percent of the influent soluble nitrogen was assimilated into new cell tissue; the remainder was mostly transformed to NO_x-N (refer ** Table 4.3-1).

Twelve percent (refer *** Table 4.3-1) of the initial total nitrogen could not be accounted for in the nitrogen mass balance procedure, the unaccounted for nitrogen was within the accuracy limits of the mass balance calculations. It is unlikely the unaccounted for nitrogen can be attributed to aerobic denitrification as the dissolved oxygen concentration was maintained at 2.5 mg/L at all times and the pH was between 6.8-7.8 which was too low for air stripping of the ammonia to have occurred. In comparison to the previous run the average time taken for the complete oxidation of the ammonia increased from 153 minutes to 175 minutes. Thus a 1.5 mg/L drop in the operational dissolved oxygen concentration increased the aeration time by nearly 15% or 22 minutes.

The online real time plots for pH and air flow continued to display some useful features that were correlated to biochemical events. Figure 4.3-4 shows a typical pH profile with the ammonia depletion feature (point 1). All the profiles were taken from track study six (TS6) DOSP 2.5 mg/L.

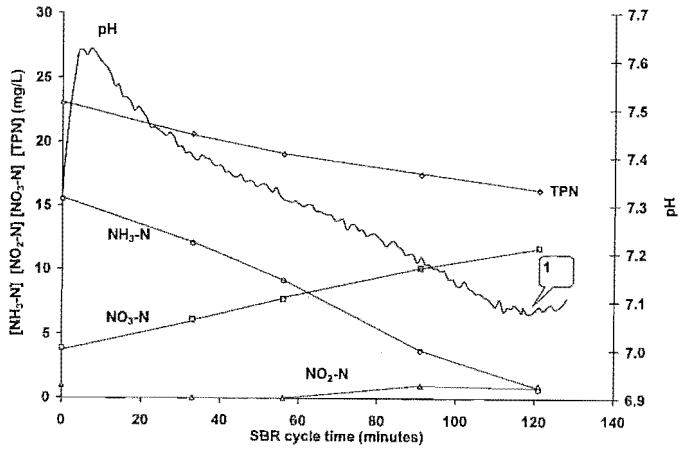


Figure 4.3-4 pH and [soluble nitrogen]

The pH profiles were consistent and the ammonia valley feature (point 1 Figure 4.3-4) was always clear and well defined. During the run the SBR completed approximately 370 cycles. The process control system using the ammonia valley detection algorithm correctly identified the valley (and terminated the aeration) in 360/370 cycles giving a successful detection rate equal to 97% reliability. The 10 cycles where the algorithm failed to detect correctly the point of ammonia depletion were due to either a flat slope following the valley or an earlier pH spike (with false trigger) caused by noise in the signal. Figure 4.3-5 shows the air flow profile with ammonia and COD data.

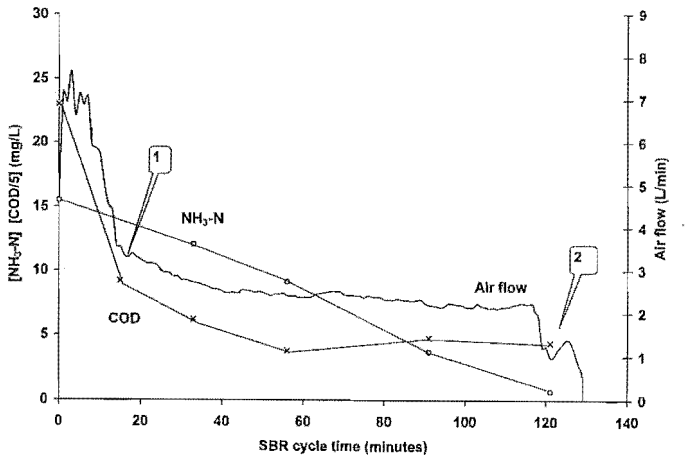


Figure 4.3-5 Air flow rate [NH_3-N] and [COD]

The depletion of COD was indicated by the transition to a level gradient (point 1 Figure 4.3-5) and ammonia depletion was indicated by a sudden fall in the air flow at the end of the cycle (point 2 Figure 4.3-5). A visual inspection of the 370 cycles resulted in an estimate that the air flow profile could have been used for determination of the point of COD and ammonia depletion in 80% and 40% of the cycles respectively.

The ammonia depletion feature remained relatively inconsistent in that the feature was not of a repetitive shape and was often not that distinct. For this reason an algorithm is unlikely to be able to reliably use the profile to detect the point of ammonia depletion as a consistent predictable shape is a prerequisite of successful automated process control. Figure 4.3-6 shows the ORP and dissolved oxygen profiles.

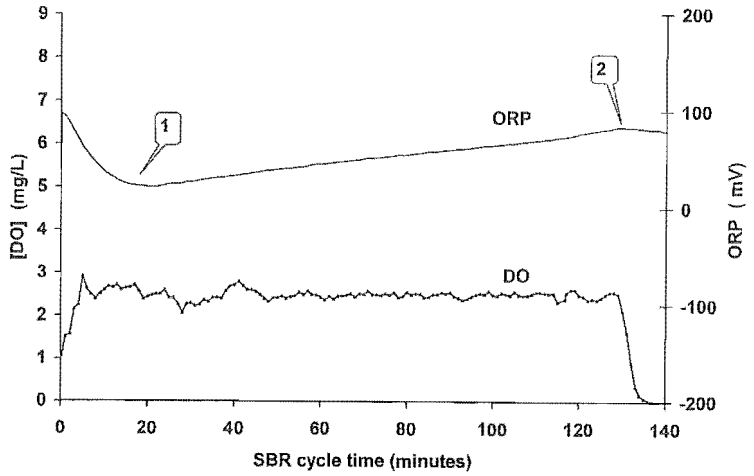


Figure 4.3-6 ORP and [DO]

The ORP profile did not show any distinguishing features that could be correlated to the depletion of nutrients. The response of the ORP does not appear to correspond directly with features on the dissolved oxygen profile (as one would expect). For example the change of the ORP from a negative to a positive slope (point 1 Figure 4.3-6) occurred 18 minutes after the initiation of aeration, also the

ORP apex (point 2 Figure 4.3-6) appeared to occur slightly before the dissolved oxygen concentration actually reached zero or before anoxic conditions had developed. Reasons for this may include the dissolved oxygen probe not accurately reflecting the true dissolved oxygen concentration (out of calibration), and/or the ORP probe itself may have been fouled slightly leading to a slow response.

4.4 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 1.0 mg/L

The reactor was operated at a dissolved oxygen set point of 1.0 mg/L and allowed to run for an acclimatisation period of 15 days. Since the SRT for this run was approximately 15 days this period was equivalent to one sludge age. Seven track studies were undertaken at dissolved oxygen set point 1.0 mg/L, the track studies were undertaken over a one-month period following the 15-day acclimatisation period. Following the switch to DOSP 1.0 mg/L the reactor displayed consistent conditions in terms of the online parameters within 3 days. The acclimatization period of 15 days was considered adequate before sampling analysis was undertaken. This section provides a summary and example of the results while Appendix A3 contains a full set of results. Figure 4.4-1 shows the [MLSS] over the duration of the run.

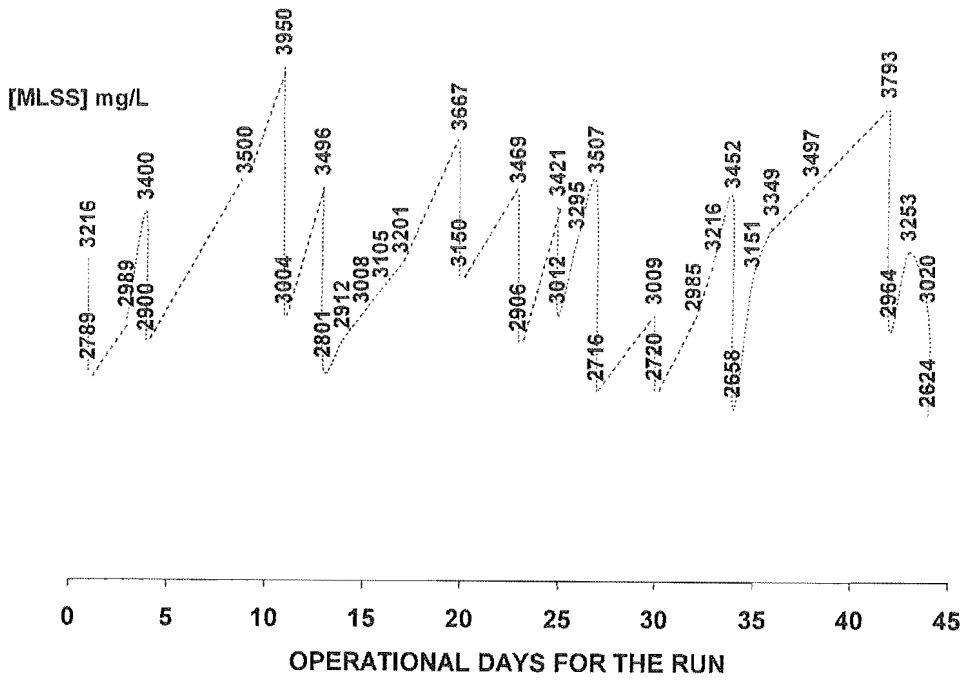


Figure 4.4-1 Mixed liquor suspended solids concentration DOSP 1.0 mg/L

The wasting rate required to keep the [MLSS] close to 3000 mg/L is illustrated in Figure 4.4-2, while Figure 4.4-3 shows the SRT of the system.

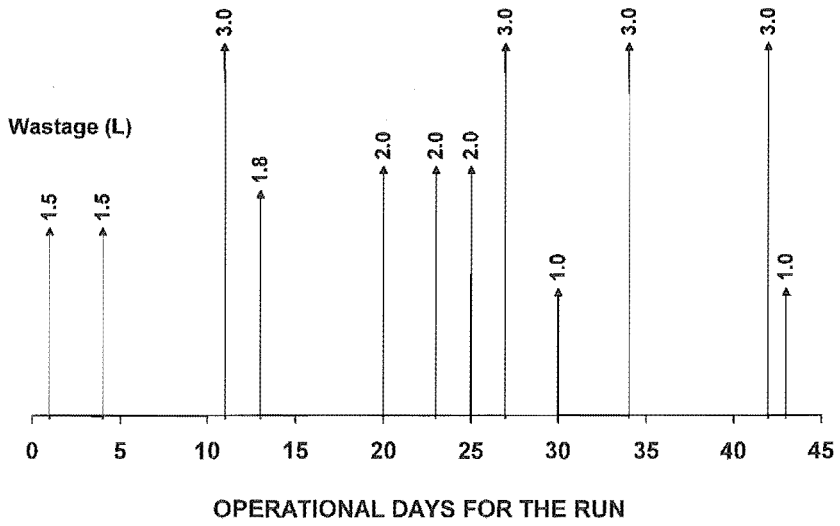


Figure 4.4-2 Mixed liquor wastage DOSP 1.0 mg/L

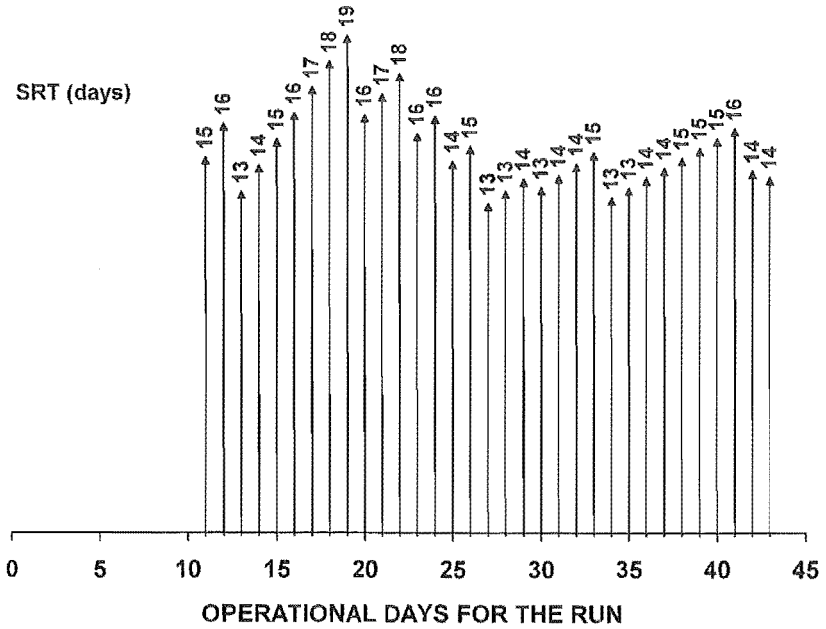


Figure 4.4-3 Solids residence time DOSP 1.0 mg/L

Table 4.4-1 provides a summary of the seven track studies undertaken at DOSP 1.0 mg/L while Table 4.4-2 shows the average values corresponding to the hydraulic residence time.

Table 4.4-1 Summary of track study data [operational dissolved oxygen] 1.0 mg/L

Parameter		Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave	
[MLSS]		mg/L	2912	3008	3105	3469	3012	3507	3793	3258	
Initial NH_3-N		mg/L	20	21	18	20	21	19	18	20	*
Final NH_3-N		mg/L	0	1	0	0	1	1	1	1	
Del NH_3-N	(A)	mg/L	19	20	18	20	20	18	17	19	
Initial NO_2-N		mg/L NO_2-N	3	2	2	3	2	2	2	2	*
Final NO_2-N		mg/L NO_2-N	6	5	5	6	4	5	6	5	
Del NO_2-N	(B)	mg/L NO_2-N	3	2	3	4	3	3	4	3	
Initial NO_3-N		mg/L NO_3-N	3	5	3	5	4	2	4	4	*
Final NO_3-N		mg/L NO_3-N	10	11	7	11	10	10	9	10	
Del NO_3-N	(C)	mg/L NO_3-N	6	6	4	6	6	8	5	6	
Nitrogen loss	(D) = (A - (B+C))	mg/L N	10	11	11	11	11	8	8	10	
Estimated assmilated nitrogen	(E)	mg/L N	2	2	2	2	5	4	2	3	
Unaccounted for nitrogen loss	(F) = (D-E)	mg/L N	8	10	9	9	6	3	6	7	
Nitrification rate		mg/L.min N	0.08	0.09	0.07	0.08	0.08	0.08	0.07	0.08	
		mg/L.min.mg MLSS	3.E-05	3.E-05	2.E-05	2.E-05	3.E-05	2.E-05	2.E-05	2.E-05	
Rate unaccounted N loss		mg/L.min N	3.E-02	5.E-02	4.E-02	3.E-02	3.E-02	1.E-02	2.E-02	3.E-02	
% Initial TN removal		%	38	41	47	38	44	33	32	39	
% TN assimilated		%	8	6	8	8	19	18	7	11	**
% Initial TN loss unaccounted		%	31	34	39	31	24	15	25	28	***
TPN Initial	(G)	mg/L N	28	31	26	31	29	26	27	28	
TPN Final	(H)	mg/L N	18	19	15	20	17	18	19	18	
TPN loss	(I) = (G-H)	mg/L N	10	12	12	11	12	8	8	10	
COD Initial	(J)	mg/L N	130	182	144	169	180	161	155	160	
COD Final	(K)	mg/L N	18	26	24	26	23	23	20	23	
COD loss	(L)=(J-K)	mg/L N	112	156	120	143	157	138	135	137	

Table 4.4-2 Summary of HRT values DOSP 1.0 mg/L

Parameter	Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave
Cycle time	minutes	264	266	277	299	289	278	306	283
HRT	days	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Cycle/day	Cycle/day	5.5	5.4	5.2	4.8	5.0	5.2	4.7	5

With reference to Table 4.4-1 the average influent soluble nitrogen was approximately 26 mg/L (not including soluble organic N, this figure composed of 20 mg/L NH_3-N, 2 mg/L NO_2-N, and 4 mg/L NO_3-N, refer * Table 4.4-1). There was significant nitrogen lost from the system which could not be accounted for via the nitrogen mass balance and there was a build up of NO_2-N suggesting a possible inhibition of the nitrification process (elevated nitrite levels often accompany aerobic denitrification activity (Ho (1994), Yoo *et al* (1999)).

Eleven percent of the influent soluble nitrogen was assimilated into new cell tissue; the remainder was mostly transformed to NO_x-N. Twenty eight percent (refer *** Table 4.4-1) of the initial total nitrogen could not be accounted for in the nitrogen mass balance procedure. The build up of NO_2-N, and the unaccounted for nitrogen loss suggests that aerobic denitrification activity was present in the system.

The time taken to complete the oxidation of the ammonia increased from 175 to 283 minutes. Thus a further 1.5 mg/L drop in the operational dissolved oxygen concentration increased the aeration time by nearly 62% or 108 minutes.

The online profiles for pH and air flow continued to provide some features that were correlated to the depletion of ammonia and COD. Figure 4.4-4 shows a typical pH profile with the ammonia valley (point 1) indicating the point of ammonia depletion, (all profiles taken from TS6 DOSP 1.0 mg/L).

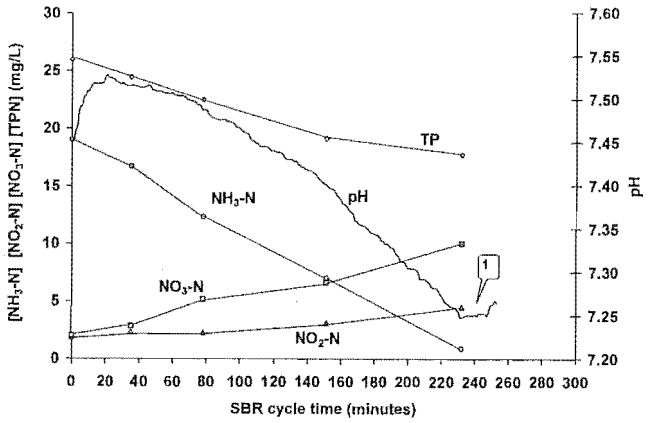


Figure 4.4-4 pH and [soluble nitrogen]

The online pH profiles consistently illustrated the ammonia valley feature, (point 1 Figure 4.4-4). The process control system correctly identified the ammonia valley in 214/228 cycles giving a successful detection rate equal to 94% reliability. Figure 4.4-5 shows a typical air flow profile with ammonia and COD data.

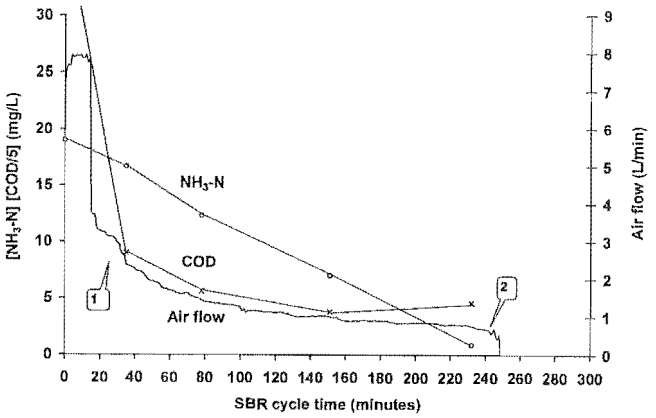


Figure 4.4-5 Air flow rate [NH_3-N] and [COD]

The depletion of COD (point 1 Figure 4.4-5) and ammonia nitrogen (point 2 Figure 4.4-5) were indicated by a transition to a level gradient and a drop in the air demand respectively. A visual inspection of the 228 cycles resulted in an estimate that the profile could have been used to identify the points of COD and ammonia depletion in 80% and 30% of the cycles respectively. The lower

operational dissolved oxygen set point resulted in the ammonia depletion feature being less distinct. Figure 4.4-6 shows the ORP and dissolved oxygen profiles.

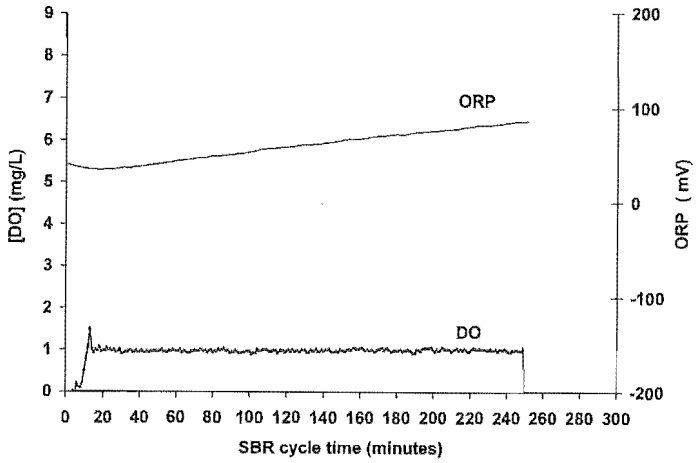


Figure 4.4-6 ORP and [DO]

As with the previous operational dissolved oxygen set points the ORP profile was devoid of features (correlated to either the transformation or the depletion of nitrogen or organic carbon) that would enable it to be used as a process control tool.

4.5 SUMMARY AND EXAMPLE OF OPERATIONAL DISSOLVED OXYGEN CONCENTRATION 0.5 mg/L

The reactor was set to a dissolved oxygen set point of 0.5 mg/L and allowed to run for an acclimatization period of 15 days. The SRT for this run was approximately 29 days thus the acclimatization period was equivalent to half a sludge age (the SRT was double the previous SRT value experienced at DOSP 1.0 mg/L). Consistent behavior (in terms of online profiles) was established within 3 days following the decrease in the DOSP from 1.0 mg/L to 0.5 mg/L. Seven track studies were undertaken at dissolved oxygen set point 0.5 mg/L. The track studies were obtained over a one-month period following the 29-day acclimatization period. This section provides a summary and example of the results while Appendix A4 contains a full set of results. Figure 4.5-1 illustrates the [MLSS] over the duration of the run.

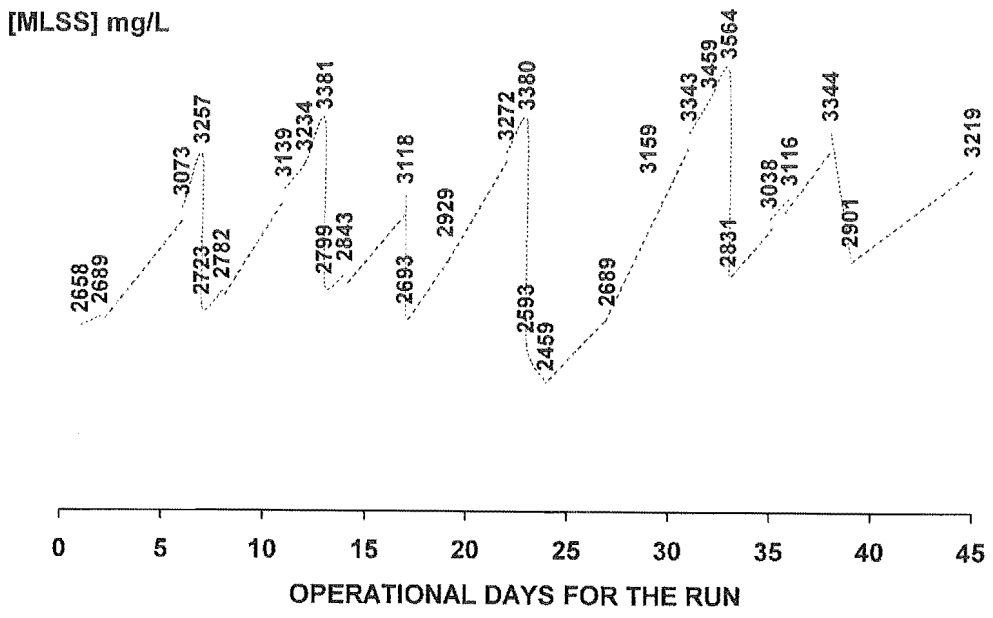


Figure 4.5-1 Mixed liquor suspended solids concentration DOSP 0.5 mg/L

The wasting rate required to keep the [MLSS] close to 3000 mg/L is illustrated in Figure 4.5-2, while Figure 4.5-3 illustrates the SRT of the system.

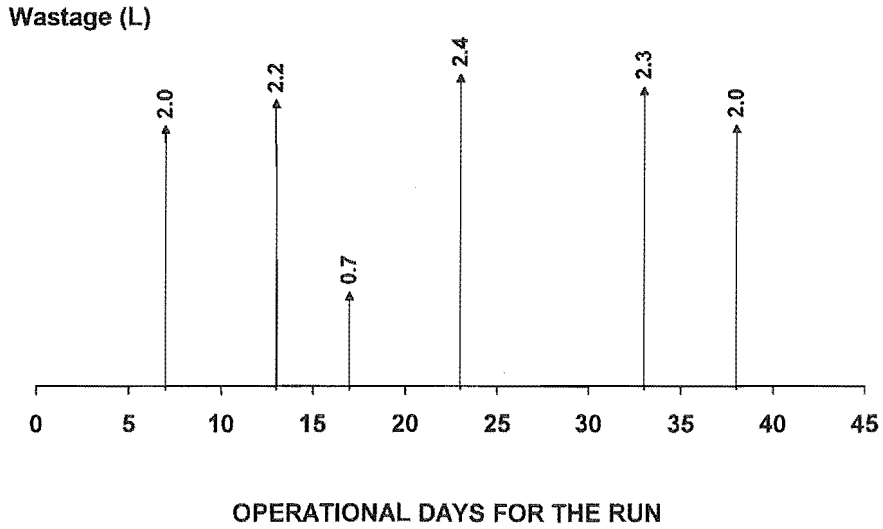


Figure 4.5-2 Mixed liquor wastage DOSP 0.5 mg/L

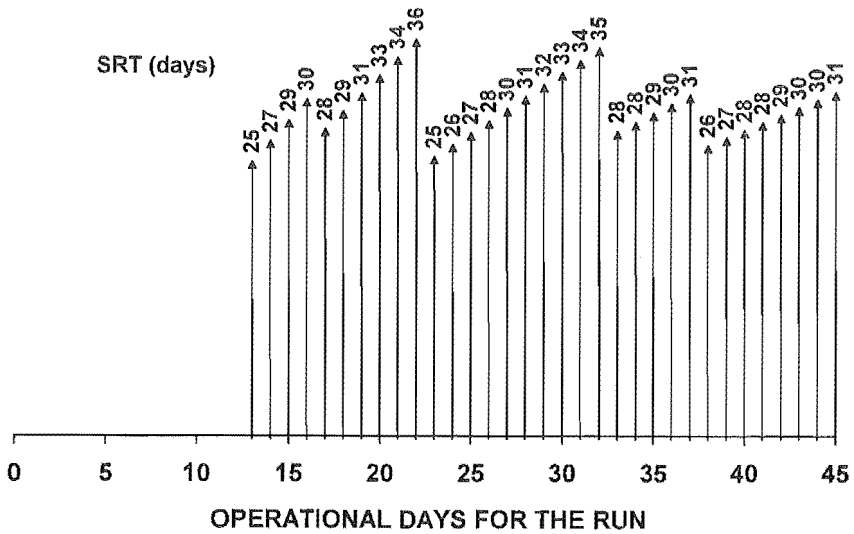


Figure 4.5-3 Solids residence time DOSP 0.5 mg/L

Table 4.5-1 provides a summary of the seven track studies undertaken at DOSP 0.5 mg/L while Table 4.5-2 illustrates the average values corresponding to the hydraulic residence time.

Table 4.5-1 Summary of track study data [operational dissolved oxygen] 0.5 mg/L

Parameter		Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave	
[MLSS]		mg/L	3160	2929	3380	2953	3343	3344	3256	3195	
Initial NH_3-N		mg/L	21	22	21	20	20	18	23	21	*
Final NH_3-N		mg/L	0	0	1	0	0	1	0	0	
Del NH_3-N	(A)	mg/L	21	22	20	20	20	17	23	20	
Initial NO_2-N		mg/L NO_2-N	5	4	4	6	5	6	5	5	*
Final NO_2-N		mg/L NO_2-N	11	10	8	11	11	10	10	10	
Del NO_2-N	(B)	mg/L NO_2-N	6	6	4	5	6	5	5	5	
Initial NO_3-N		mg/L NO_3-N	3	1	2	1	2	2	2	2	*
Final NO_3-N		mg/L NO_3-N	5	3	3	2	3	2	2	3	
Del NO_3-N	(C)	mg/L NO_3-N	2	2	1	1	1	0	1	1	
Nitrogen loss	(D) = (A - (B+C))	mg/L N	12	14	15	14	13	12	17	14	
Estimated assmilated nitrogen	(E)	mg/L N	2	3	3	4	2	5	3	3	
Unaccounted for nitrogen loss	(F) = (D-E)	mg/L N	11	11	12	10	11	7	14	11	
Nitrification rate		mg/L.min N	0.05	0.06	0.05	0.05	0.05	0.04	0.06	0.05	
		mg/L.min.mg MLSS	2.E-05	2.E-05	2.E-05	2.E-05	2.E-05	1.E-05	2.E-05	2.E-05	
Rate unaccounted N loss		mg/L.min N	3.E-02	3.E-02	3.E-02	2.E-02	3.E-02	1.E-02	3.E-02	3.E-02	
% Initial TN removal		%	43	52	54	52	49	46	57	50	
% TN assimilated		%	6	11	11	15	9	19	12	11	**
% Initial TN loss unaccounted		%	38	41	43	37	41	28	46	40	***
TPN Initial	(G)	mg/L N	31	30	30	29	29	29	32	30	
TPN Final	(H)	mg/L N	19	16	15	15	16	16	15	16	
TPN loss	(I) = (G-H)	mg/L N	13	14	15	14	13	13	17	14	
COD Initial	(J)	mg/L N	159	171	136	152	161	106	170	151	
COD Final	(K)	mg/L N	25	23	26	28	23	20	23	24	
COD loss	(L)=(J-K)	mg/L N	134	148	110	124	138	86	147	127	

Table 4.5-2 Summary of HRT values DOSP 0.5 mg/L

Parameter	Units	TS1	TS2	TS3	TS4	TS5	TS6	TS7	Ave
Cycle time	minutes	434	441	421	470	424	452	471	445
HRT	days	0.6	0.6	0.6	0.7	0.6	0.6	0.7	0.6
Cycle/day	Cycle/day	3.3	3.3	3.4	3.1	3.4	3.2	3.1	3

With reference to table 4.5-1 the average influent soluble nitrogen was approximately 28 mg/L (not including soluble organic N, this figure composed of 21 mg/L NH_3-N, 5 mg/L NO_2-N, and 2 mg/L NO_3-N, refer * Table 4.5-1). Eleven percent (refer ** Table 4.5-1) of the influent soluble nitrogen was assimilated into new cell tissue; the remainder was mostly transformed to NO_x-N in particular there was a significant increase in the NO_2-N concentration. Forty percent (refer *** Table 4.5-1) of the initial total nitrogen could not be accounted for in the nitrogen mass balance procedure.

The significant increase in the amount of unaccounted for nitrogen and the increase in nitrite nitrogen would suggest an increase (relative to DOSP 1.0 mg/L) in aerobic denitrification activity at the 0.5 mg/L dissolved oxygen level. There was a significant increase in the time required for the oxidation of the ammonia. In comparison to the previous run the time taken for the complete oxidation of the ammonia increased from 283 minutes to 445 minutes. Thus a 0.5 mg/L drop in the operational dissolved oxygen concentration increased the aeration time by nearly 57% or 162 minutes.

The online real time plots for pH and air flow displayed some useful features that were correlated to biochemical events. Figure 4.5-4 shows a typical pH profile, all the profiles were taken from TS1 DOSP 0.5 mg/L.

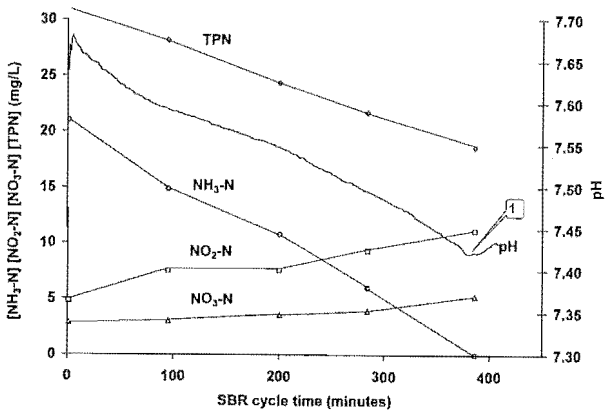


Figure 4.5-4 pH and [soluble nitrogen]

The pH profiles were consistent and the ammonia valley feature, (Point 1 Figure 4.5-4) was well defined. During the run the SBR completed 145 cycles. The process control system using the ammonia valley detection algorithm correctly identified the valley in 133/145 cycles giving a successful detection rate equal to 92% reliability. Figure 4.5-5 shows the air flow profile along with the profiles for ammonia and COD.

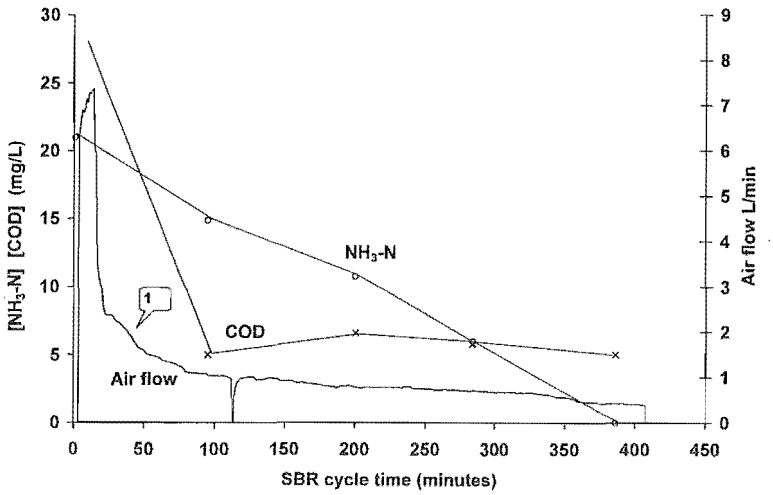


Figure 4.5-5 Air flow rate, [NH_3-N] and [COD]

The depletion of COD (point 1 Figure 4.4-5) was indicated by a transition to a somewhat level gradient (There was no feature identifying the point of ammonia depletion in this figure). A visual inspection of the 145 cycles resulted in an estimate that the profile could have been used to identify the point of COD and ammonia depletion in 80% and 15% of the cycles respectively. The results suggest that the ammonia depletion feature becomes less apparent as the operational dissolved oxygen set point is lowered. Figure 4.5-6 illustrates the ORP and dissolved oxygen profiles.

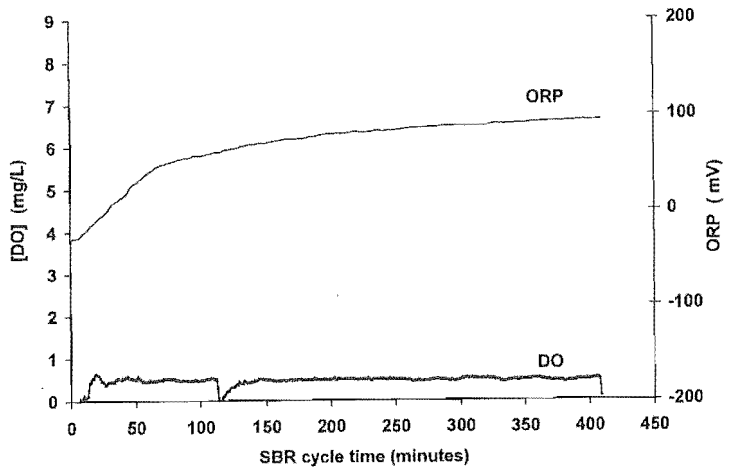


Figure 4.5-6 ORP and [DO]

ORP failed to show any distinguishing features that would enable it to be used as a process control tool.

Chapter 5.0 DISCUSSION

5.1 (Objective 1) Confirm the presence of aerobic denitrification activity.

Operation of the reactors at the 4.0 mg/L and 2.5 mg/L dissolved oxygen level resulted in a 95-100% transformation of ammonia nitrogen to nitrate nitrogen. At these dissolved oxygen concentrations the presence of nitrite nitrogen was < 1 mg/L and the nitrogen mass balance procedure was able to account for approximately 90% of the influent nitrogen. That is 90% of the influent nitrogen went to known forms and could be accounted for with the mass balance procedure. However once the dissolved oxygen concentration was lowered to 1.0 mg/L and 0.5 mg/L the nitrogen mass balance identified significant losses from the system. At these dissolved oxygen levels 30% - 40% of the influent nitrogen could not be accounted for with the nitrogen mass balance procedure. That is the loss of ammonia nitrogen could not be balanced by an increase in nitrite, nitrate, or assimilated nitrogen.

The nitrogen mass balance typically assumed ~10% of the influent nitrogen was assimilated during each cycle. This estimate is higher than that reported by Patureau *et al* (1998) who found the amount of nitrogen lost to assimilation in a nitrifying sequencing batch reactor was around 1%. The removal of nitrogen from the system under aerobic conditions suggests aerobic denitrification activity was present, (volatilization of ammonia was not possible as the pH was too low at around 7.0).

While there was minimal nitrite nitrogen present when the dissolved oxygen concentration was maintained at 4.0 mg/L and 2.5 mg/L the nitrite nitrogen levels were as high as 6 mg/L and 11 mg/L when the dissolved oxygen concentration was lowered to 1.0 mg/L and 0.5 mg/L respectively. The presence of elevated nitrite levels is another indicator that aerobic denitrification was occurring. Ho

(1994) suggested that aerobic denitrification may be accompanied by the inhibition of the second step of nitrification involving the oxidation of nitrite to nitrate. Elevated levels of nitrite nitrogen are common in aerobic denitrification processes and have been reported by other researchers such as Randal and Buth (1984), Hanaki and Wantawin (1990), Ho (1994), Munch *et al* (1996), Yoo *et al* (1999), and Delgenes and Patureau (2004b)).

A likely explanation for the nitrite build up is that *Nitrobacter* can be inhibited by low dissolved oxygen concentrations. With reference to double Monod kinetics the half saturation coefficient for dissolved oxygen is 0.25-0.5 mg/L for *Nitrosomonas*, this is lower than that of 0.72-2.84 for *Nitrobacter.* ((Randal *et al* (1992), Munch *et al* (1996), Helmer and Kunst (1998)).

This means that *Nitrobacter* is more susceptible to low dissolved oxygen concentrations than *Nitrosomonas,* and operation at a dissolved oxygen concentration of 1.0 mg/L and 0.5 mg/L could have inhibited the *Nitrobacter* activity leading to a build up of nitrite. Munch *et al* (1996) operated a lab scale aerobic denitrification SBR and found that nitrite accumulated within the system when the oxygen concentration was maintained lower than the half saturation coefficient of nitrobacter.

In summary the presence of aerobic denitrification activity at dissolved oxygen concentrations of 1.0 mg/L and below was supported by the development of elevated nitrite levels and from mass balance calculations.

5.2 (Objective 2) Elucidate some operational aspects of aerobic denitrification, in particular comment on the nitrification, denitrification, and sludge production rates.

5.2.1 Nitrification rates

With reference to Figure 5.2-1 the biokinetic nitrification rates were considerably lower when the operational dissolved oxygen was ≤ 1.0 mg/L (the range required for aerobic denitrification). A traditional nitrification process is likely to be operated at > 2.0 mg/L and is likely to have a nitrification rate three times that of a system operated around the 0.5 mg/L aerobic denitrification range.

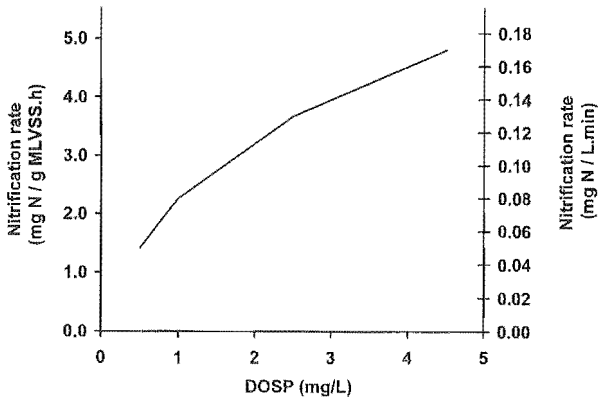


Figure 5.2-1 Nitrification rate versus dissolved oxygen concentration

The decrease in the nitrification rate translates directly into increased aeration time for aerobic denitrification processes. Table 5.2-1 and Figure 5.2-2 illustrate the increase in aeration time required as the operational dissolved oxygen concentration was lowered.

Table 5.2-1 Aeration time relative to dissolved oxygen concentration

Dissolved oxygen set point	Average aeration time	Relative drop in dissolved oxygen concentration	~Relative increase in treatment time
mg/L	minutes	mg/L	%
4.0	153		
2.5	175	1.5	14
1.0	283	1.5	60
0.5	445	0.5	60

The rate of nitrification experienced at the 0.5 mg/L aerobic denitrification level in this experimental work corresponds well with that reported by Demoulin *et al* (2001) who investigated the 90,000 p.e. aerobic denitrification plant in Potsdam Germany. They reported a nitrification rate of 1.1 mg N/g MLSS.h. This experimental work had a slightly higher value at 1.2 mg N/g MLSS.h. (1.4 mg N/g MLVSS.h, tests showed the biomass was approximately 84% volatile).

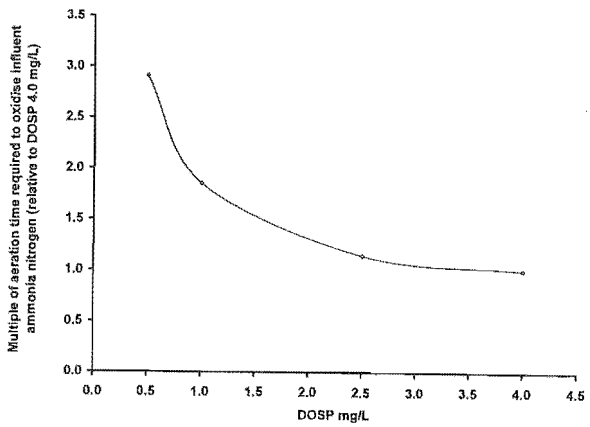


Figure 5.2-2 Extension in aeration time required to oxidise ammonia nitrogen (relative to DOSP 4.0 mg/L)

Munch *et al* (1996) reported a nitrification rate of 1.47 mg N/g MLVSS.h for an aerobic denitrification system in which the average dissolved oxygen concentration during the aeration phase was 1.2 mg/L.

Metcalf and Eddy (2001) reported the rates of both nitrification and denitrification in aerobic denitrification processes are likely to be a function of the reaction kinetics, floc size, floc density, floc structure, rbCOD loading and bulk DO concentration. Because of the complex physical factors the process is still to be modeled accurately. However Metcalf and Eddy (2001) reported nitrification rates for the aerobic denitrification process to be lower than conventional processes. This is thought to be due to the lower dissolved oxygen concentrations and because only a portion of the nitrifying bacteria contained within the flocs are active.

Metcalf and Eddy (2001) reported typical nitrification rates for conventional plants being in the order of 0.78 – 21 mg N/g MLVSS.h. It would appear that the nitrification rates for aerobic denitrification facilities are at the extreme lower end of the values reported for conventional processes.

5.2.2 Denitrification rates

Full denitrification was not achieved in this work. The aerobic denitrification process only managed ~50% nitrogen removal (including any assimilation). If the 50% nitrogen removal value is converted into a rate it would equate to approximately 0.71 mg N/g MLVSS.h

It is possible the incomplete nitrogen removal was a result of a low COD/N ratio and/or the complexity of the wastewater organic carbon compounds. Research by Third (2004) investigated aerobic denitrification within sequencing batch reactors and suggested it was a heterotrophic process which relied on the storage of carbon polymers (for use as intra-cellular carbon) for the reduction of oxidized nitrogen. Third (2004) found that the quantity and types of storage polymers depended upon the quantity and type of organic carbon present in the feed. That is simple organic carbon compounds such as glucose or acetate (not typically present in wastewater but present in synthetic experimental feed) are

more easily stored as polymers and produce simple polymers such as PHB. Barker and Dold (1996), Wentzel and Ekama (1997) suggested a COD/N ratio >12 is required to adequately support the denitrification process while Third (2004) suggested a COD/N ratio (in influent feed) of >10 to achieve complete aerobic denitrification. This research used a domestic wastewater that typically had a COD/N ratio of around 5. It is possible the low COD/N ratio combined with aspects such as raw wastewater producing storage polymers that did not easily hydrolyze and release "reducing power" may be contributing factors to the incomplete nitrogen removal achieved in this research.

With respect to the values reported by Demoulin *et al* (2001) the German Potsdam facility is required to comply with E.C. directive 91/271 which requires strict effluent standards in particular for nutrients. Since the nitrification rates for the Potsdam aerobic denitrification facility were essentially the same as those experienced in this work, assuming a 90% nitrogen removal objective for the Potsdam plant the rate of denitrification can be estimated as a value of 0.9 x 1.1 mg N/g MLSS.h = 1.0 mg N/g MLSS.h (or approximately 1.2 mg N/g MLVSS.h).

Metcalf and Eddy (2001) reported values for conventional denitrification range from 2.5 - 3.8 mg N/g MLVSS.h for a single sludge anoxic reactor under non limiting conditions (at 20 ^{o}C) and 0.56-1.6 mg N/g MLSS.h for systems using endogenous carbon sources. Values for aerobic denitrification processes have yet to be established however Metcalf and Eddy (2001) reported aerobic denitrification process would have lower denitrification rates than conventional processes because of substrate consumption in the aerobic portion of flocs.

It would appear that the rate of denitrification for the aerobic denitrification process is less, probably around half of that experienced in traditional separate stage anoxic denitrification facilities. From an experimental perspective there are conflicting reports with respect to aerobic denitrification rates. Patureau *et al*

(1998) suggested the rate of aerobic denitrification will largely be limited by the rate of nitrification at the low dissolved oxygen concentration. Neef *et al* (1996) indicated that micro-organisms capable of aerobic denitrification may have slower denitrification rates than anoxic denitrifying bacteria. However Delgenes and Patureau (2004a) identified numerous strains of microorganisms able to aerobically denitrify. Upon further examination they found the aerobic denitrifying performances of the consortium were comparable to traditional anoxic denitrifying performances.

A summary of the nitrification and denitrification rates for both traditional and aerobic denitrification facilities is shown in Table 5.2-2. These values are approximates sourced from this experimental work and calculated from Munch *et al* (1996), Metcalf and Eddy (1991), and Demoulin *et al* (2001).

Table 5.2-2 Comparison of biochemical transformation rates between conventional and aerobic denitrification processes.

	~Nitrification rate mg N/g MLSS.h	~Denitrification rate mg N/g MLSS.h
Aerobic denitrification process	1.0	1.0
Conventional N/DN process	<21	<4

With reference to Table 5.2-2 the lower rates of biochemical transformation for the aerobic denitrification process suggest the overall treatment reactor volume will need to be larger. This finding is supported by Metcalf and Eddy (2001) who reported aerobic denitrification was only suitable for processes with sufficient volume to accommodate the lower nitrification and denitrification rates. That is aerobic denitrification will require a longer detention time and larger treatment reactors than a conventional process.

This conflicts with some reports from full scale aerobic denitrification facilities which suggest an overall saving in treatment capacity. For example Collivignarelli and Bertanza (1999) partitioned off the equivalent of 2,500 p.e. of a full-scale 440,000 p.e. facility and converted it into an aerobic denitrification process. A two year trial showed the aerobic denitrification process offered a possible 20% saving in treatment tank volume compared to the conventional process (when results are translated on a flow weighted basis). This conclusion is also supported by the research of Demoulin *et al* (1997) who compared the efficiency of the aerobic denitrification process to a conventional nitrification denitrification process. Parallel operations lasting one year were undertaken at the Austrian GroBarl WWTP in 1995. It was found that the aerobic denitrification process demonstrated superior treatment efficiency when operated at the same loading conditions as the conventional process. Both nitrogen and phosphorus removals were consistently around 30% higher in the aerobic denitrification batch process. It was estimated that the aerobic denitrification process offered a volumetric saving of about 30% when compared to the conventional treatment technology.

However it is difficult to compare the results of Collivignarelli and Bertanza (1999) and Demoulin *et al* (1997) with the experimental data from this research as their papers appear to lack firm design data (such as comparative biochemical transformation rates). Another important variable that has been overlooked by Collivignarelli and Bertanza (1999) and Demoulin *et al* (1997) is the need for additional post aeration facilities to oxidise any remaining nitrite nitrogen from the main treatment process. This may be necessary in situations were elevated effluent nitrite levels could be problematic. For example elevated nitrite nitrogen levels can be particularly troublesome for plants that use chlorination for disinfection as nitrite is readily oxidized by chlorine requiring 4g chlorine/g NO_2-N (Metcalf and Eddy 2001). Additional aeration facilities to oxidise (periodic) elevated nitrite levels may also need to be considered when sizing / designing an aerobic denitrification facility.

In summary this experimental work suggests the nitrification and denitrification rates for aerobic denitrification are significantly lower than those of conventional separate stage processes. It appears that savings in terms of achieving opposing reactions in the same time/space are likely to be offset somewhat by the reduced rate of biochemical transformation. While it is possible aerobic denitrification may offer opportunities for simplification of the treatment process (i.e. less recycled flow) the experimental results obtained in this research suggest it is unlikely aerobic denitrification will offer a reduction in the size or number of reactors required. These results appear to contradict reports from some full scale plants which suggest aerobic denitrification may offer the potential for treatment tank volumetric savings.

5.2.3 Sludge production rates

Table 5.2-3 illustrates the normalized sludge production rates. It shows the mass of sludge created per volume of wastewater treated. The aerobic denitrification process produced significantly less waste sludge than the traditional nitrification process.

Table 5.2-3 Normalized sludge production

DOSP	Wastage (L)	Cycles	*Wasted Solids (mg)	**WW Treated (L)	Normalized Waste (mg/L) (kg/m^3)
4.0	57	420	171000	1680	102
2.5	42	370	124200	1480	84
1.0	25	228	74400	912	82
0.5	12	145	34800	580	60

*Assuming average wastage [] = 3000mg/L ** 4 L wasted / cycle x number of cycles

It should be noted that the higher dissolved oxygen set points only nitrified the wastewater while the aerobic denitrification process also denitrified. Therefore the true savings in sludge production arising from the aerobic denitrification process will be greater than suggested by Table 5.2-3. That is the nitrification

only systems would also have a sludge contribution from subsequent anoxic facilities (required for denitrification). Further research is required to determine the sludge production rates in an optimized aerobic denitrification process (one that achieves full denitrification).

There is little reference in the literature as to the sludge production rates for the aerobic denitrification process. However assuming the aerobic denitrification process uses a shortened denitrification (nitritation type) pathway Turk and Mavinic (1986) and Turk and Mavinic (1987) found this nitrogen removal pathway can result in lower biomass yields. Delgenes and Patureau (2004b) also suggested a shortened denitrification pathway achieved through the control of dissolved oxygen should result in less biomass production. Stouthamer *et al* (1997) investigated some of the microorganisms responsible for aerobic denitrification and found that some like *Thiosphaera pantotropha* produced a lower growth yield.

5.3 (Objective 3) Comment on the requirements for air relative to conventional separate stage nitrification denitrification processes.

Table 5.3-1 shows the total amount of air required to oxidise the influent ammonia nitrogen.

Table 5.3-1 Total air required for ammonia oxidation

Dissolved oxygen set point mg/L	Average air required L air / mg NH_3-N	Average air flow rates L/min
4.0	2.3	2.8
2.5	2.0	2.0
1.0	2.9	1.8
0.5	3.5	1.3

With reference to Table 5.3-1 the 4.0 mg/L DOSP required more air per unit of ammonia oxidized than the 2.5 mg/L DOSP because of excessive aeration and inefficiencies at the 4.0 mg/L level. The increase in the amount of air required at DOSP 1.0 mg/L and 0.5 mg/L is due to inhibition of the nitrification process caused by the low dissolved oxygen concentrations.

The data suggests a traditional nitrification process run at ~ 2.5 mg/L would require ~ half as much air per unit of ammonia oxidized compared to an aerobic denitrification process run at 0.5 mg/L.

With respect to the average flow rates required to reach the dissolved oxygen set points it can be seen the 0.5 mg/L aerobic denitrification process required approximately half the air flow rate of the traditional 2.5 mg/L nitrification process.

Thus it appears as if the aerobic denitrification process may require twice as much air supplied at half the air flow rate, (relative to a traditional nitrification process run at a dissolved oxygen concentration of 2.5 mg/L). This might translate into higher overall aeration costs for the aerobic denitrification process as efficiencies in terms of smaller blowers or the number of units required may not offset the cost in terms of $/unit of air required.

Experiences from full scale facilities suggest a reduction in aeration requirements. For example Hayward (1998) investigated an aerobic denitrification and phosphorus removal plant at Cabooltura (Australia). He said the aerobic denitrification process had the ability to minimize the operational costs associated with supplementary chemical treatment and aeration (reduced aeration times were reported). However it should be noted that the SBR type plant also incorporated an online real time control system at the time of transferring to an aerobic denitrification process. It is possible that the reported

aeration savings were a result of the new control system also providing increased efficiency.

Heinen and Norgaard (1998) reported results from full-scale facilities modified to incorporate nitrogen removal through aerobic denitrification. Specifically they noted the low dissolved oxygen concentration required for the process ensured that existing aeration facilities were usually sufficient in upgraded plants, while they expected proposed new facilities would require less oxygenation equipment. Pedersen *et al* (2003) reported on the conversion of the industrial wastewater treatment plant at the CPKelco ApS pectin plant in Denmark. The industrial WWTP is one of the largest in Denmark and was converted from a conventional nitrification/denitrification process to a nitritation-denitritation process. That is the process was converted to one of ammonium oxidation to nitrite followed by controlled reduction of nitrite to N_2. They reported the shortened pathway process decreased the oxygen required for oxidation by 25%.

The development of a 2,500 p.e. aerobic denitrification trial facility within a larger 440,000 p.e. plant by Collivignarelli and Bertanza (1999) allowed operating data to be obtained over a two year period. They undertook a cost evaluation of both conventional and aerobic denitrification facilities. Based on costs calculated in Italian lire it was found the construction of conventional facilities required an additional 10% capital investment along with an ongoing 30% higher operational cost per year. Specifically it was found that a 50% saving in the electrical energy expenditure could be attained with an aerobic denitrification process.

From an experimental perspective Yu *et al* (1998) reported that appropriate online control combined with the savings attainable from an aerobic denitrification shortened nitritation pathway could result in aeration energy savings of up to 45%. Abeling and Seyfried (1992) reported on aeration savings resulting from the use of a shortened nitritation pathway. They found nitritation required only

75% of the oxygen resources compared to full pathway nitrification. This was supported by Delgenes and Patureau (2004b) who reported a possible 25% reduction in theoretical air requirements for nitritation followed by nitrite type denitrification. Stross (2000) reported on the CANON process (refer literature review) in which nitrification is limited to nitrite type nitrification. He reported a 63% decrease in the total air requirements.

In summary, the experimental data indicated the aerobic denitrification process required a lower air flow rate and this may provide opportunities in terms of smaller blowers (or less units) and corresponding lower capital costs. However the process also required twice as much air in total (per unit of ammonia oxidised). This may indicate the aeration running costs for an aerobic denitrification system could be higher.

5.4 (Objective 4) Identify the dissolved oxygen conditions necessary for aerobic denitrification and for its optimisation.

A major variable influencing the rate of aerobic denitrification appears to be the dissolved oxygen concentration as shown in Table 5.4-1.

Table 5.4-1 Effect of dissolved oxygen concentration on aerobic nitrogen losses

Dissolved oxygen set point mg/L	Average % of influent nitrogen lost aerobically
4.0	7% *
2.5	10% *
1.0	26%
0.5	40%

** The nitrogen mass balance procedure was an approximation. Limitations of the [MLSS] testing procedure meant that a precise determination of assimilation was not possible, losses here may be within accuracy limits of the mass balance.*

There was a drop in aerobic denitrification from 40% at a dissolved oxygen concentration of 0.5 mg/L to 0-7% at a dissolved oxygen concentration of 4.0 mg/L. The nitrogen losses at the 1.0 and 0.5 mg/L dissolved oxygen concentrations are classified as "aerobic denitrification losses".

It is important to note that the losses can probably be ascribed to both traditional anoxic denitrification and aerobic denitrification. That is a combined effect of aerobic denitrification and classic anoxic denitrification, refer literature review 1.2-1.4).

The aerobic denitrification activity appeared to become suppressed in environments where the dissolved oxygen concentration was above 1.0 mg/L. Nitrogen losses increased as the dissolved oxygen concentration was lowered to 0.5 mg/L suggesting 0.5 mg/L was closer to an optimum than 1.0 mg/L.

The research attempted to operate at a set point of 0.3 mg/L however the hardware was unable to reliably measure and control the dissolved oxygen concentration at this level. The experimental hardware was limited to the use of traditional dissolved oxygen probes which were not suited to this application. As the aeration system relied upon a reading from the probe to adjust the amount of air supplied a small drift in the probe reading at the low set point could result in a (proportionately) significant reduction in aeration. That is the probe could read ~0.3 mg/L when the actual conditions were anoxic, in this situation the aeration system would assume the set point of 0.3 mg/L had been reached and the air flow rate was reduced to ~zero. There was also a degree of instability as a result of operating a nitrification system at such a low dissolved oxygen concentration. That is the nitrification process became significantly inhibited most probably by the lack of dissolved oxygen. Dissolved oxygen concentrations below 0.5 mg/L are reported to result in considerable inhibition of the nitrification process (Metcalf and Eddy (2001)).

While this research suggested the optimum dissolved oxygen concentration appeared to be around 0.5 mg/L research by Third (2004) suggests the optimum dissolved oxygen concentration for aerobic denitrification is unlikely to be a fixed value, rather it will depend upon variables such as the biomass concentration and the release of reducing power in terms of the ability to hydrolyze stored carbon polymers.

The elevated nitrite and nitrate levels and absence of effluent ammonia nitrogen at the 0.5 mg/L dissolved oxygen set point in this work may suggest the optimum (in this instance) was lower than 0.5 mg/L. Researchers such as Munch *et al* (1996), Demoulin *et al* (1997), Yoo *et al* (1999), and Collivignarelli and Bertanza (1999) found that dissolved oxygen concentrations above the aerobic denitrification optimum resulted in the effluent containing higher concentrations of NO_2-N and NO_3-N while dissolved oxygen levels too low resulted in higher NH_3-N concentrations in the effluent.

Munch *et al* (1996) suggested a dissolved oxygen value of 0.5 mg/L was suitable to achieve a nitrification rate equal to the denitrification rate ensuring complete aerobic denitrification. However they only reported the 0.5 mg/L dissolved oxygen level as a theoretical value and did not operate at that level. Instead they established nitrification and denitrification rates at higher dissolved oxygen concentrations and then determined a theoretical dissolved oxygen concentration that could produce the same rate of nitrification and denitrification. This was done by combining a Monod type kinetic expression for the rate of nitrification and an IAWQ model for the rate of denitrification.

Pochana *et al* (1997) developed a mathematical model to determine the optimum dissolved oxygen concentration for aerobic denitrification. The model was based on the hypothesis of diffusion limitations in activated sludge flocs. They found

that a dissolved oxygen concentration of 0.2 mg/L may result in incomplete nitrification with elevated effluent ammonia concentrations along with complete denitrification of any oxidized ammonia. At a dissolved oxygen concentration of 0.5 mg/L the model found that nitrification would improve but a build up of nitrite and nitrate could be expected. Thus the model essentially predicted the optimum dissolved oxygen concentration would be somewhere between 0.2-0.5 mg/L. The model also predicted that aerobic denitrification could achieve over 90% nitrogen removal at very low dissolved oxygen concentrations (0.2 mg/L) where as at higher dissolved oxygen concentrations (>1mg/L) the aerobic denitrification reaction would be strongly inhibited.

In general the experimental findings obtained in this research complement those of other researchers including Pochana *et al* (1997). That is this research found the 0.5 mg/L set point had elevated effluent nitrite and nitrate concentrations while the 0.3 mg/L set point had residual ammonia nitrogen, (no data presented as system unstable). The data also illustrated an inhibition of aerobic denitrification at dissolved oxygen concentrations above 1.0 mg/L.

A review of the literature would suggest the optimum dissolved oxygen concentration (range) for the activated sludge aerobic denitrification process has not been determined experimentally. Reported optimum values are either theoretical or from studies involving cultures (with plans to extend this to more complex systems). Attempts to experimentally isolate the optimum dissolved oxygen range have been imprecise. In the late 1990's a central figure in the attempts to determine the optimum aerobic denitrification dissolved oxygen concentration was Jurg Keller of the Advanced Wastewater Management Centre Queensland Australia. Keller was involved with the research of Pochana *et al* (1997), Pochana and Keller (1999) and with the earlier work by Munch *et al* (1996). In experimental terms Pochana and Keller (1999) attempted to validate earlier theoretical work. This was partially successful however as with other

studies the optimum dissolved oxygen concentration (range) was not determined. They worked with dissolved oxygen concentrations down to 0.8 mg/L and found that aerobic denitrification rates continued to increase down to and possibly beyond those concentrations (lab-scale SBR activated sludge process).

With respect to studies involving cultures attempts have been made to identify the specific optimum conditions for aerobic denitrifiers within culture studies with the aim of transferring this knowledge to experiments with activated sludge processes. For example Heijnen and Van Loosdrecht (2004) are currently undertaking research at the Delft university clean technology institute to determine the process conditions which lead to optimal aerobic nitrogen elimination rates in wastewater treatment processes. This research is based upon earlier experiments with the model organism *Thiosphaera pantotropha* which have indicated the specific optimum conditions for which aerobic denitrification is likely to occur.

Other culture studies include those of Chen *et al* (2003) who undertook experiments with cultures of *Pseudomonas aeruginosa* (ATCC 9027) and demonstrated an approximate linear increase in aerobic denitrification activity as the dissolved oxygen concentration was lowered from 1.3 mg/L to 0.1 mg/L. The rate at 1.3 mg/L was only 1/8 of the maximum rate (1.7 mmol/g of cells.h). In order to measure the dissolved oxygen concentration at such low levels their work required the use of optical sensors that could accurately determine very low dissolved oxygen concentrations based upon oxygen-quenched luminescence.

Patureau *et al* (2000) extended earlier work with culture studies and trialed an aerobic denitrifier organism mixture within an alternating aerobic/anoxic process (in the presence of nitrate). They evaluated the aerobic denitrifying performance at various dissolved oxygen concentrations and found that aerobic denitrification activity was present up to oxygen saturation conditions (7 mg/L dissolved

oxygen), however the denitrifying enzymes became increasingly active below a 0.35 mg/L threshold.

From a full scale perspective Goronzy *et al* (1997) examined several processes incorporating aerobic denitrification. The important aspect was ensuring that the process loading was sufficient so that for at least half of the aeration phase the oxygen demand exceeded the oxygen supply capability of the aeration system, such that the bulk dissolved oxygen concentration was <1.0 mg/L. This provided the opportunity for substantial nitrogen removal via aerobic denitrification.

Hayward (1998) investigated an aerobic denitrification SBR wastewater treatment facility in Caboolture South Australia. To achieve full ammonia transformation and effluent total nitrogen concentrations under 5 mg/L the aeration system was operated so that the first half of the aeration phase had a dissolved oxygen concentration below 0.5 mg/L. Following that the dissolved oxygen concentration was allowed to slowly climb to an ultimate concentration of 2 mg/L at the end of the aeration cycle (DO breakthrough). Hayward (1998) found that maintenance of the dissolved oxygen below 0.5 mg/L was key to ensuring low effluent nitrogen levels via aerobic denitrification (NO_x-N < 2.5 mg/L). Short periods of dissolved oxygen concentrations as high as 2 mg/L at the Caboolture plant did not appear to inhibit or affect the aerobic denitrifiers.

Thus while the aerobic denitrification process requires a low dissolved oxygen concentration it would appear that "short" periods of high DO to oxidise remaining ammonia may be acceptable. Demoulin *et al* (1997) demonstrated that once established an aerobic denitrification process could continue for a limited period in the presence of high dissolved oxygen concentrations however they also found that continued operation at high dissolved oxygen concentrations required a significant re-acclimatization period (~10 days) before removal efficiencies were "fully restored". Munch *et al* (1996) found that "extended" operation at high

dissolved oxygen concentrations resulted in long term damage to the aerobic denitrifying microorganisms, that is the removal efficiencies were not fully restored following a period of extended operation at high dissolved oxygen concentrations.

In summary the general consensus is that the activated sludge aerobic denitrification process has a dissolved oxygen concentration optimum somewhere close to but below 0.5 mg/L. While stable operation at 0.5 mg/L was achieved in this research the elevated nitrite and nitrate levels at 0.5 mg/L suggested the optimum was probably below this. Reliable experimental data for the 0.3 mg/L dissolved oxygen set point was not obtained.

5.5 (Objective 5) Comment on the need for soluble organic carbon for the removal of nitrogen in the aerobic denitrification process.

This research demonstrated the removal of nitrogen under aerobic conditions continued at approximately the same rate even when soluble organic carbon sources had been depleted. This is depicted in Figure 5.5-1 which shows the rate of nitrogen removal (in terms of TPN) as well as the soluble organic carbon concentration measured as COD.

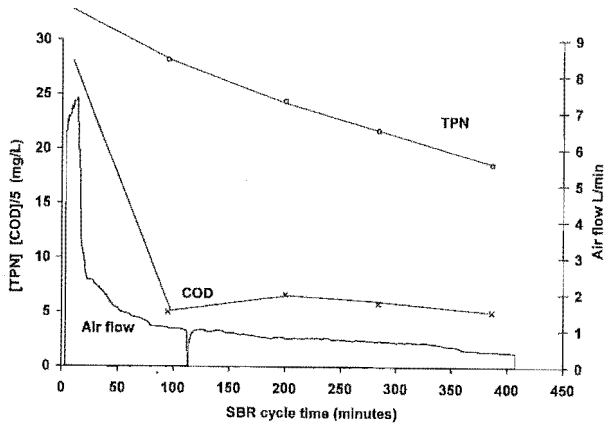


Figure 5.5-1 Cycle illustrating nitrogen removal rate versus soluble organic carbon availability

Two explanations for the nitrogen loss include autotrophic denitrification, and heterotrophic denitrification possibly using stored intracellular carbon.

Researchers to suggest that wastewater nitrogen reduction may be achieved autotrophically include Strous *et al* (1997), Helmer and Kunst (1998), Dijkman and Strous (1999), Stross (2000), and Holman (2000). For example Helmer and Kunst (1998) proposed that newly formed NO_2-N may act as the electron acceptor in the autotrophic conversion of ammonia to N_2. They demonstrated 90% aerobic nitrogen removal from a largely autotrophic micro-organism population degrading landfill leachate without addition of any organic substrate. Holman (2000) also demonstrated aerobic nitrogen losses in the absence of soluble organic carbon in a lab experiment using synthetic wastewater. In this case the rate of nitrogen removal did not diminish once the carbon source was depleted. In some instances near total nitrogen removal was achieved in an aerobic process without (measurable) soluble organic carbon. (Refer to literature review for the work of Dijkman and Strous).

Researchers to suggest that aerobic nitrogen reduction may be due to heterotrophic activity include Patureau *et al* (1998), Zhao *et al* (1999), and Pochana and Keller (1999). Patureau *et al* (1998) identified a particular strain of *M aerodenitrificans* capable of aerobic denitrification, they reported that *M aerodenitrificans* has a high affinity for acetate (making it heterotrophic). Zhao *et al* (1999) reported that the addition of acetate significantly improved their aerobic denitrification rates and speculated that this was due to improved heterotrophic denitrification. Pochana and Keller (1999) ran a sequencing batch reactor for 45 days and showed aerobic denitrification activity was significantly improved during periods when the feed was spiked with readily degradable acetate. From this they concluded that aerobic nitrogen reduction was undertaken by heterotrophic microorganisms. It should be noted however that increased anoxic denitrification or traditional heterotrophic activity has also been shown to occur following

acetate addition. For example Bilanovic *et al* (1999) found the addition of acetate as a carbon source helped eliminate accumulated nitrite in an anoxic/aerobic reactor. Gerber *et al* (1986) and Tam *et al* (1992) also found that acetate gave higher anoxic denitrification rates than either methanol or glucose. Henze (1989) found that the denitrification rate using wastewater as the carbon source in a traditional separate stage denitrification process was only one third of the value obtained when acetate or methanol was available.

Another explanation for nitrogen loss in the apparent absence of soluble carbon may be heterotrophic denitrification using stored intracellular carbon. The sequencing batch reactor is characterized by fluctuations in substrate concentrations over time (feast famine conditions). Research by Third (2004) at the University of Murdoch Western Australia has found that some bacteria can adapt strategies to cope with the large fluctuations in electron donor/acceptor concentrations. For example some microorganisms have been found to be able to store soluble organic substrate as polymers. Aerobic denitrification research by Third (2004) suggests that the SBR can select microorganisms which have metabolic strategies such as storage capabilities. When these microorganisms are cyclically exposed to high concentrations of substrate but limited electron acceptor they are able to take in substrate far in excess of the amount required for growth and respiration. This excess uptake of substrate can be converted into a storage polymer such as PHB (poly-B-hydroxybutyrate) as illustrated in Figure 5.5-2. The PHB is essentially an energy reserve that is subsequently used when an electron acceptor such as oxygen or nitrate nitrogen becomes available.

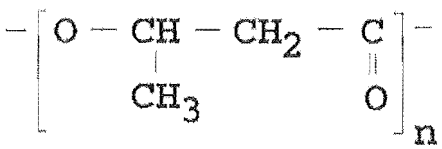


Figure 5.5-2 PHB (poly-B-hydroxybutyrate)

Third (2004) correlated PHB concentrations and aerobic denitrification rates and found denitrification ceased when stored carbon in terms of PHB was diminished suggesting aerobic denitrification may be a heterotrophic process using stored intracellular carbon. Data presented at the SBR3 conference Noosa Queensland Australia March 2004 suggests that under suitable conditions up to 70% of the soluble acetate can be converted to PHB. At this stage the trials have been limited to a lab scale SBR run on synthetic wastewater, (with acetate as the carbon source). The type of storage polymer formed depends upon the carbon source. For example acetate is known to form PHB, the use of propionate and acetate will yield PHV, glucose tends to yield glycogen. There is little data on polymer storage with respect to aerobic denitrification systems operated with raw domestic wastewater. To complement the lab scale experiments the University of Murdoch is currently developing a 26 cubic meter pilot plant as well as a full-scale experiment.

If municipal wastewaters are shown to inhibit the aerobic denitrification process (due to a lack of simple organic carbon compounds) it is possible that the inclusion of prefermenters to transform complex organics to simple organic compounds may alleviate the problem.

At this stage it is thought polymer formation is "favoured" by the use of simple organic compounds such as acetate as compared to the more complex organic compounds found in raw wastewater. If acetate is favoured this may explain the reported increase in aerobic denitrification rates following the addition of acetate by researchers such as Pochana and Keller (1999). It would also explain the results obtained by Holman (2000) in which an aerobic denitrification process treating synthetic wastewater (including acetate) within a lab scale SBR achieved ~98% nitrogen removal while a similar process run with this research but with raw domestic wastewater has achieved much lower nitrogen removal rates ~50%.

The carbon storage-heterotrophic explanation is also supported by some full-scale aerobic denitrification facilities. For example Demoulin *et al* (2001) reported on the Potsdam wastewater treatment plant in Germany (90,000 p.e.) in which aerobic denitrification is achieved via internal floc denitrification using carbon stored through biosorption. They reported the low dissolved oxygen concentration of the process minimizes the use of substrate carbon by oxic metabolism.

With respect to the data obtained with this experimental work Figure 5.5-1 shows a constant rate of nitrogen removal (~ 0.95 mg N/g MLVSS.h). It is possible the nitrogen reduction rate would decrease during a cycle as the stored organic carbon was depleted or the rate of nitrogen removal would have been higher at the start of a treatment cycle when soluble organic carbon was present. Third (2004) found that one variable governing the rate of aerobic denitrification was the release of reducing power from storage polymers. It is possible the use of (complex relative to synthetic feed) domestic wastewater results in complex storage polymers that provide a slow sustained release via polymer hydrolysis. That is it is possible the polymers were not depleted within the cycle lengths of this research. Third (2004) also found that the aerobic denitrification process had a higher nitrogen removal rate after the carbon had been taken up as a storage polymer. This would explain why nitrogen removal rates were not greater at the start of the cycles in this work when soluble organic carbon was present.

While the mechanism behind the nitrogen removal remains somewhat unclear, the ability to remove nitrogen in the apparent absence of soluble organic carbon may offer economic advantages in terms of organic and operational savings. Semi-treated wastewater may not need to be exposed to raw incoming wastewater, (carbon source), or supplied with an expensive external carbon source such as methanol. Traditional ("relatively" high dissolved oxygen concentration) processes can require the addition of an external carbon source when the insitu organic carbon supply is insufficient. Bilanovic *et al* (1999)

undertook a comparison of different external carbon sources for denitrification and found the cheapest source by far was methanol. However some US$0.011 of methanol was still required for the denitrification of each m^3 of wastewater containing 30 mg/L of NO_3-N. This means that the use of an external carbon source for denitrification is still an expensive operation in the wastewater industry.

A review of the literature indicates that quantification of the carbon requirements for the aerobic denitrification process have not been conclusively determined. Yu *et al* (1998) obtained full denitrification with a COD/NO_x-N ratio of ~3 when their aeration phase was restricted to nitrite type nitrification. This compares to the research of Tam *et al* (1992) who proposed a COD/NO_x-N ratio of ~6 for traditional denitrification. Delgenes and Patureau (2004b) proposed a possible 40% reduction in the organic carbon requirement for denitrification following nitrite type nitrification. Patureau is currently undertaking research (2004) that will quantify the organic carbon savings from a (low dissolved oxygen controlled) nitrite type nitrification aerobic denitrification process. Pedersen *et al* (2003) reported on the conversion of the industrial wastewater treatment plant at the CPKelco ApS pectin plant in Denmark to a nitritation/denitritation process in which nitrite type nitrification-denitrification decreased the carbon required for reduction by 40% (when compared to the previous conventional nitrification/denitrification process).

In summary while some researchers have demonstrated that aerobic denitrification may be achieved autotrophically under certain circumstances. The general consensus is that the process is heterotrophic requiring the presence of organic carbon. It is also generally agreed that the process has a lower stoichiometric requirement for organic carbon due to the low dissolved oxygen concentration resulting in nitrification inhibition and shortened pathway nitrification-denitrification. It is also felt that intra-cellular carbon storage can play

a role due to the low dissolved oxygen concentrations minimizing the use of substrate carbon by oxic metabolism and/or microorganism metabolic storage strategies resulting from batch type processes. The experimental work demonstrated the ability of aerobic denitrification to remove nitrogen from wastewater without the need for supplementary carbon, thus there exists a possibility for savings in operational costs in terms of the opportunity to remove nitrogen with less dependence on organic carbon. The mechanism behind the nitrogen removal (in the absence of soluble carbon) and "quantification" of the requirements for organic carbon remain to be "conclusively" determined.

5.6 (Objective 6) Confirm if the online profiles have unique features with respect to the aerobic denitrification process, in particular the ammonia elbow on the ORP profile and the ammonia valley on the pH profile. Correlate these online features with measured biochemical events such as the depletion of organic carbon or ammonia nitrogen.

5.6.1 ORP

In an aerobic nitrifying environment electrons are transferred from the ammonia nitrogen to oxygen which acts as the electron acceptor. At the same time the ORP profile shows a positive slope as electrons are also transferred from the ORP reference cathode to the oxygen (which has a greater positive potential). As the ammonia is depleted and the flow of electrons from the ammonia nitrogen to the oxygen diminishes this would also be expected to affect the rate of electron flow from the ORP probe. Effectively more oxygen should be available to act as electron acceptors for the ORP reference cathode and this could theoretically be expected to cause an elbow or increase in the positive ORP gradient.

Some researchers have in fact made a correlation between the ORP ammonia elbow and the point of ammonia depletion with the implication being the increase in ORP and the depletion of the ammonia are directly related (i.e. the change in

ORP is due to changes in oxidative reductive potential resulting from the depletion of ammonia nitrogen). For example Yu *et al* (1998) suggested the elbow resulted from ammonia depletion in an A/O process as shown in (Figure 5.6.1-1).

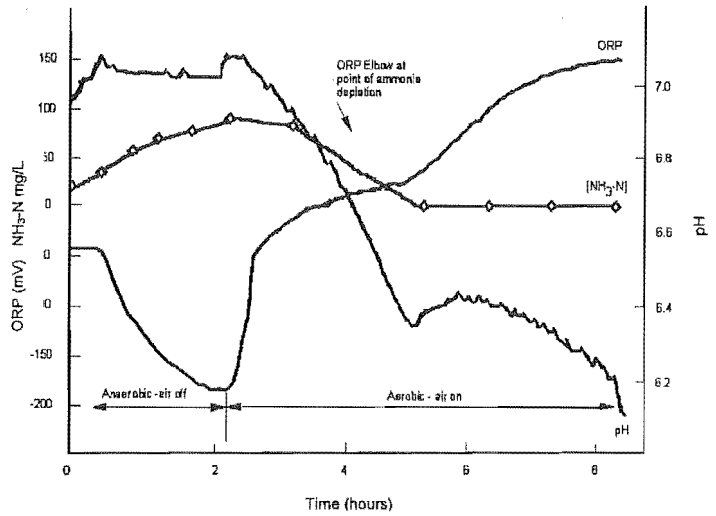


Figure 5.6.1-1 illustration of ORP elbow in an A/O process. (Figure Adapted from Yu *et al* (1998)

Another example of a correlation between the ORP elbow and the point of ammonia depletion was evident in the work of Ra *et al* (2000). They operated an aerobic-anoxic SBR process treating piggery wastewater and identified the ORP elbow at the point of ammonia depletion. They then used ORP to terminate aeration. In this instance they detected the ORP plateau that follows the elbow feature (Figure 5.6.1-2).

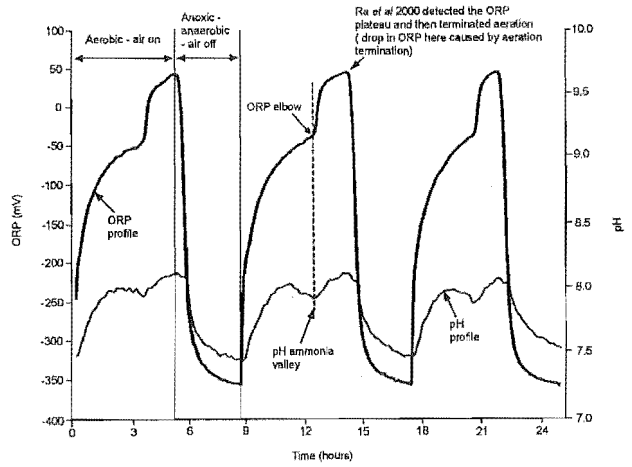


Figure 5.6.1-2 illustration of ORP elbow in an A/O process. (Figure Adapted from Ra *et al* (2000)

Research by Holman and Wareham (2003) indicated the existence of an ORP elbow at the point of ammonia depletion within an aerobic denitrification process treating readily biodegradable synthetic wastewater Figure 5.6.1-3.

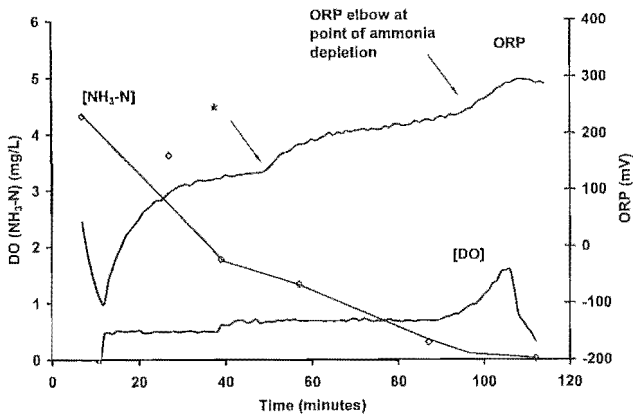


Figure 5.6.1-3 illustration of ORP ammonia elbow in an aerobic denitrification process, Holman and Wareham (2003), (note anoxic phase for first 10 minutes). *First ORP elbow resulted from organic carbon depletion, not shown.

The existence of an ORP ammonia elbow during the aerobic sludge digestion process was also proposed by Wareham *et al* (1993) and Wareham *et al* (1994) as illustrated in Figure 5.6.1-4.

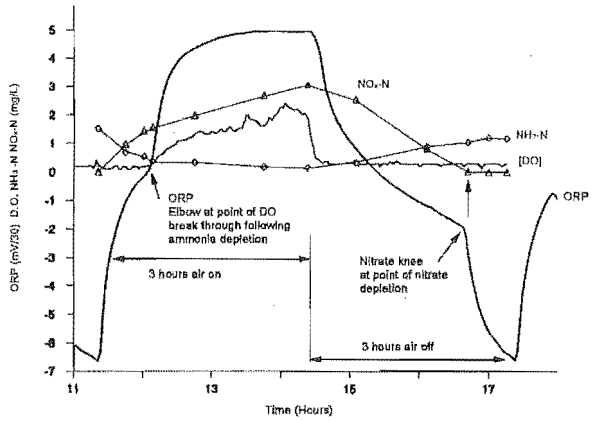


Figure 5.6.1-4 Illustration of ORP elbow in aerobic sludge digestion process. (Figure adapted from Wareham *et al* 1993).

However in all the cases cited the dissolved oxygen concentration was allowed to vary and find its own level. Figure 5.6.1-5 however shows a typical ORP profile within an aerobic denitrification environment held at a fixed dissolved oxygen concentration (0.5 mg/L). As can be seen dissolved oxygen breakthrough was suppressed (as a result of the dissolved oxygen set point control system) and the ORP showed no elbow at the point of ammonia depletion.

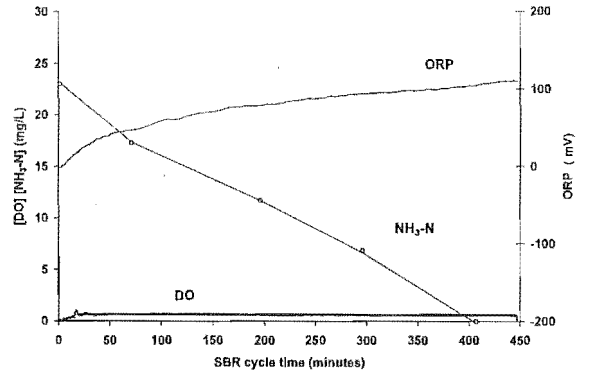


Figure 5.6.1-5 illustration of absence of ORP ammonia elbow when dissolved oxygen concentration maintained at a consistent level (taken from TS7 DOSP 0.5 mg/L).

As the ORP ammonia elbow does not appear when the dissolved oxygen is held at a fixed concentration it appears that the ORP ammonia elbow results exclusively from the dissolved oxygen breakpoint. That is the ORP elbow is a

response to dissolved oxygen concentration changes rather than a direct response to the depletion of ammonia itself. For exarnple if the aeration system allowed the dissolved oxygen concentration to breakthrough following the depletion of ammonia then the ORP would show a corresponding elbow and increase at the point of dissolved oxygen increase.

In this work the ammonia elbow failed to appear for both the traditional nitrification process when the dissolved oxygen concentration was maintained at 4.0 mg/L and 2.5 mg/L and the aerobic denitrification process when the dissolved oxygen concentration was maintained at 1.0 mg/L and 0.5 mg/L.

The ORP dependence on the dissolved oxygen concentration may be due to the logarithmic interrelationship between DO and ORP (section 1.6) and the strong electron acceptance potential of the dissolved oxygen. Collivignarelli and Bertanza (1999) reported the ORP value in the aerobic denitrification process was determined by the O_2/OH^- equilibrium, as well as NO_3^-/NH_4^+ NO_2^-/NH_4^+ etc. However these experimental results suggest the O_2/OH^- equilibrium is probably the dominant parameter such that in the presence of dissolved oxygen changes in the other parameters do not result in detectable changes in the value of ORP. In practical terms this means the ORP ammonia elbow probably results exclusively from the DO breakpoint and it is misleading to imply the elbow is a direct response to ORP changes resulting from ammonia depletion.

The dominance of dissolved oxygen and the effective suppression of an ORP feature resulting directly from the depletion of ammonia probably raises doubts as to the usefulness of the ORP profile in aerobic-aerated processes. Skepticism of ORP measurements in aerobic processes has been expressed by other researchers including Al-Ghusain *et al* (1994) and Csikor *et al* (1996) who suggested the need for better online real time parameters such as pH. Cecil (2003) reported on the development of a redox process control system at the

Odense City wastewater treatment plant in Denmark. Redox was clearly shown to indicate the point of nitrate depletion during an anoxic phase. However redox provided no useful information during the aerobic phases and an ammonium sensor was necessary to determine the point of ammonia depletion during aeration.

Thus while it would be possible to use the ORP elbow feature to identify the point of ammonia depletion in a variable dissolved oxygen concentration system it appears that a more direct pathway would be to use the dissolved oxygen breakpoint feature itself.

5.6.2 pH

The nitrification process was known to produce a pH profile with an ammonia depletion feature (ammonia valley Hao and Huang (1996)). One objective of the experimental work was to determine if the pH profile was also applicable to the aerobic denitrification process; that is, did the ammonia valley identify the point of ammonia depletion in a low dissolved oxygen aerobic denitrification process.

The results of this research found the pH profile provided a consistent and reliable indication of the point of ammonia depletion for both the traditional nitrification and the aerobic denitrification processes. The main pH feature termed the ammonia valley was present at all dissolved oxygen levels. With reference to Figure 5.6.2-1 the beginning of aeration caused a rise in pH (between points 1 and 2); probably due to CO_2 stripping from the system caused by the initiation of aeration. After the initial increase the pH decreased again between points 2 and 3, caused by nitrification and the consumption of alkalinity as part of the nitrification process (7.14 mg HCO_3 consumed per mg of ammonia). At point 3, the pH curve shows the feature termed "ammonia valley" signifying the point at which ammonia is essentially depleted and nitrification has

finished. An illustration of a pH profile from TS7 DOSP 0.5 mg/L is provided in Figure 5.6.2-1

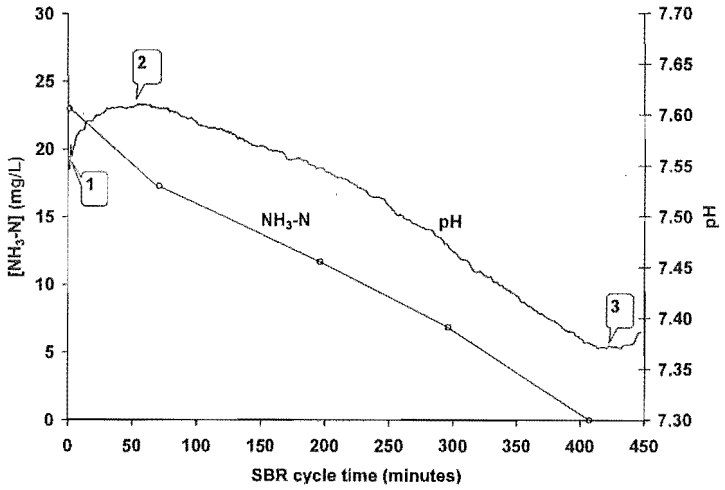


Figure 5.6.2-1 typical pH profile, (aeration starts at time = 0)

The essential shape and features of the pH profile were the same for both the traditional nitrification and aerobic denitrification processes; however aerobic denitrification produced a pH profile of half the magnitude, that is the pH scale had a maximum 0.8 unit and maximum 0.4 unit difference for the nitrification and aerobic denitrification processes respectively. This is quite possibly linked to a shortened pathway nitrification-denitrification process consuming less alkalinity in the aerobic denitrification process (section 1.2). Full pathway denitrification also returns 3.5 mg/L of alkalinity per mg of nitrogen reduced. It is possible some alkalinity was returned to the process via the aerobic denitrification process and this may have acted as a buffer.

5.6.3 Dissolved oxygen [DO]

As the control system maintained a fixed dissolved oxygen concentration the profile provided no information apart from the concentration itself. There were no features that correlated to the depletion of biochemical parameters.

5.6.4 Air flow rate

As the control system adjusted the air flow to maintain a fixed dissolved oxygen concentration the air flow rate profile essentially equated to the air demand profile. An illustration of an air flow profile taken from TS7 DOSP 0.5 mg/L is provided in Figure 5.6.4-1.

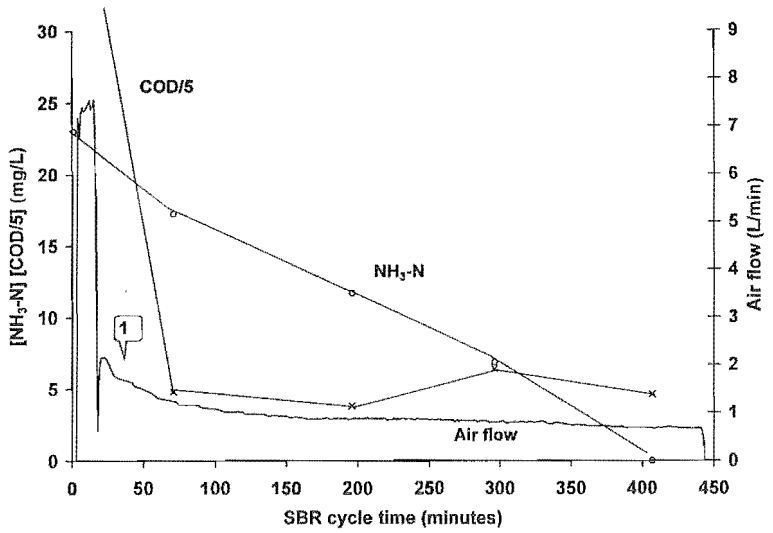


Figure 5.6.4-1 typical air flow profile

The air demand profile was expected to indicate events such as the depletion of organic carbon or ammonia nitrogen as theoretically these events would result in a fall in the oxygen demand. The research found the air demand profile provided an indication of the point of (readily available) organic carbon depletion (point 1) in 80% of the cycles. The point of ammonia exhaustion was also evident in 15-40% of the cycles (not evident in figure 5.6.4-1). The lower detection rates occurred in the runs in which the DOSP was decreased (the aerobic denitrification range). The profile was applicable to both the traditional nitrification process and the aerobic denitrification process, that is the essential elements of the profile were there in both cases. The features appeared as sudden drops in the air flow.

In summary the research findings suggest ORP does not provide any features that can be correlated to biochemical events within either the nitrification or the aerobic denitrification processes. The previously identified ammonia depletion elbow is probably a response to dissolved oxygen concentration changes (and is reliant upon a breakpoint in the dissolved oxygen concentration). There is therefore no ORP ammonia elbow when a system is operated at a fixed dissolved oxygen concentration. The implication made by some researchers that the change in ORP is related to changes in oxidative reductive potential resulting from the depletion of ammonia nitrogen is probably misleading-incorrect.

The pH profile provided a useful ammonia depletion feature that was consistently present over a range of operating conditions including those required for aerobic denitrification, (The magnitude of the feature was approximately half for the aerobic denitrification process).

The air demand profile did provide an indication of the point of organic carbon depletion; there was also periodically a feature indicating the point of ammonia depletion however this feature did not appear reliably under all operational conditions.

5.7 (Objective 7) Develop and demonstrate control algorithms that use online features to control the aerobic denitrification process, (i.e. indirectly detect the biochemical events). In doing so demonstrate the reliability of pH and ORP control algorithms based upon relative rather than absolute values.

5.7.1 ORP

ORP failed to provide any features that could be correlated to biochemical events under fixed dissolved oxygen conditions. As such the ORP profiles were of no

further use for control of either the nitrification or aerobic denitrification processes.

5.7.2 pH

The pH profile provided a feature at the depletion of the ammonia nitrogen (ammonia valley) as illustrated in Figure 5.6.2-1. In order to detect the ammonia valley an algorithm was developed in which the second derivative of pH was calculated (algorithm based upon relative rather than absolute values). This essentially equated to calculating the slope of the pH curve (dpH/dt) and then calculating the change in slope over defined time periods (d^2pH/dt^2). For example, the average slope of the pH profile over a 30-minute period would be determined (every six seconds) and when the second derivative changed beyond some specific set point (typically set at 0.001) the control system identified the event as the occurrence of the feature termed the ammonia valley and terminated the aeration cycle, that is the air was switched off and the reactor put into a settle phase. It was demonstrated that 92-99% of all cycles were able to be controlled by the algorithm. This detection rate corresponds well with a similar software system known as the Evolving Fuzzy Neural Network (EfuNN) system developed by the University of Otago and Waste Solutions Ltd (both located in Dunedin New Zealand). The EfuNN system obtained a 96% successful detection rate for DO breakpoint determination with a laboratory SBR treating synthetic wastewater (Cohen *et al* (2003)). In this research the lower detection rates occurred when the DOSP was decreased. Thus pH was demonstrated as a monitoring and control tool for both the traditional nitrification and aerobic denitrification processes. A description of the algorithms is given in Appendix B4.

5.7.3 Dissolved oxygen [DO]

As the control system maintained a fixed dissolved oxygen concentration the profile provided no information apart from the concentration itself. There were no

features that correlated to the depletion of biochemical parameters and the profile was of no use for process control purposes.

5.7.4 Air flow rate (effectively air demand)

The air demand profile contained up to two features that were correlated to the depletion of (readily biodegradable soluble) COD and the depletion of ammonia nitrogen (Figure 5.6.4-1). The experimental work showed 80% of cycles provided profiles that would have enabled an algorithm to detect the point of COD depletion while as little as 15 % of cycles showed a clear ammonia depletion feature making the point of ammonia depletion unsuited for detection by an algorithm. No air flow algorithms were developed in this experimental work.

Chapter 6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The conclusions have been incorporated into the summary sections associated with each fulfilled objective; however to reiterate, the following conclusions can be drawn from this research.

- The presence of aerobic denitrification activity at dissolved oxygen concentrations of 1.0 mg/L and below was supported by the development of elevated nitrite levels and from nitrogen mass balance calculations.

- This experimental work suggests the nitrification and denitrification rates for aerobic denitrification are significantly lower than those of conventional separate stage processes. Nitrifying bacteria are known to be inhibited by the low dissolved oxygen concentrations. It is also thought that only a portion of the nitrifying bacteria contained within flocs are active in low DO systems. The rate of denitrification is lower as denitrification is limited to the anoxic zones of floc particles. Factors such as reduced anoxic floc area and substrate consumption in the aerobic portion of the floc act to reduce the denitrification rate (Met Calf and Eddy (2001)).

- It appears that savings in terms of achieving opposing reactions in the same time/space are likely to be offset somewhat by the reduced rate of biochemical transformation. While it is possible aerobic denitrification may offer opportunities for simplification of the treatment process (i.e. less recycled flow) the experimental results obtained in this research suggest it is unlikely aerobic denitrification will offer a reduction in the size or number of reactors required. These results appear to contradict reports from some full-scale plants which suggest aerobic denitrification may offer the potential for treatment tank volumetric savings.

- Calculated on the basis of a unit of sludge created per unit of wastewater treated the results suggest the aerobic denitrification process offers a lower sludge production rate. Further research is required to determine the sludge production rates for an "optimized" aerobic denitrification processes (that is an aerobic denitrification process that is achieving full denitrification). There is little reference in the literature as to the sludge production rates for the aerobic denitrification process.

- The experimental data indicated the aerobic denitrification process required a lower air flow rate and this may provide opportunities in terms of smaller blowers (or less units) and corresponding lower capital costs. However the process also required twice as much air in total (per unit of ammonia oxidized). This may indicate the aeration running costs for an aerobic denitrification system could be higher.

- The general consensus is that the aerobic denitrification process has a dissolved oxygen concentration optimum somewhere close to but below 0.5 mg/L. While stable operation at 0.5 mg/L was achieved in this research the elevated nitrite and nitrate levels at 0.5 mg/L suggested the optimum was probably below this. Reliable experimental data for the 0.3 mg/L dissolved oxygen set point was not obtained. Metcalf and Eddy (2001) state that present models for the aerobic denitrification process are inaccurate (further research is required), however DO concentrations for the aerobic denitrification process are reported as being between 0.1 mg/L and 0.4 mg/L.

- While some researchers have demonstrated that aerobic denitrification may be achieved autotrophically under certain circumstances. The general consensus is that the process is heterotrophic requiring the presence of

organic carbon. It is also generally agreed that the process has a lower stoichiometric requirement for organic carbon due to the low dissolved oxygen concentration resulting in nitrification inhibition and shortened pathway nitrification-denitrification. It is also felt that intra-cellular carbon storage can play a role due to the low dissolved oxygen concentrations minimizing the use of substrate carbon by oxic metabolism and/or microorganism metabolic storage strategies resulting from batch type processes. The experimental work demonstrated the ability of aerobic denitrification to remove nitrogen from wastewater without the need for supplementary carbon, thus there exists a possibility for savings in operational costs in terms of the opportunity to remove nitrogen with less dependence on organic carbon. The mechanism behind the nitrogen removal (in the absence of soluble carbon) and "quantification" of the requirements for organic carbon remain to be "conclusively" determined.

- The research findings suggest ORP does not provide any features that can be correlated to biochemical events within either the nitrification or the aerobic denitrification processes. The previously identified ammonia depletion elbow is probably a response to dissolved oxygen concentration changes (and is reliant upon a breakpoint in the dissolved oxygen concentration). There is therefore no ORP ammonia elbow when a system is operated at a fixed dissolved oxygen concentration. The implication made by some researchers that the change in ORP is related to changes in oxidative reductive potential resulting from the depletion of ammonia nitrogen is probably misleading-incorrect. As ORP failed to provide any features that could be correlated to biochemical events under fixed dissolved oxygen conditions the profiles were of no further use for control of either the nitrification or aerobic denitrification processes.

- The shape and features of the pH profile were the same for both the traditional nitrification and aerobic denitrification processes. The profile provided a useful ammonia depletion feature (ammonia valley) that was consistently present over a range of operating conditions including those required for aerobic denitrification.

- Aerobic denitrification produced a pH profile of half the magnitude, that is the pH scale had a maximum 0.8 unit and maximum 0.4 unit difference for the nitrification and aerobic denitrification processes respectively. This is quite possibly linked to a shortened pathway nitrification-denitrification process consuming less alkalinity in the aerobic denitrification process.

- In order to detect the ammonia valley an algorithm was developed in which the second derivative of pH was calculated. The control system identified the feature termed the ammonia valley and terminated the aeration cycle, that is the air was switched off and the reactor put into a settle phase. It was demonstrated that 92-99% of all cycles were able to be controlled by the algorithm. The lower detection rates occurred when the DOSP was decreased. Thus pH was demonstrated as a monitoring and control tool for both the traditional nitrification and aerobic denitrification processes.

- The air demand profile contained up to two features that were correlated to the depletion of (readily biodegradable soluble) COD and the depletion of ammonia nitrogen. The experimental work showed 80% of cycles provided profiles that would have enabled an algorithm to detect the point of COD depletion while as little as 15 % of cycles showed a clear ammonia depletion feature making the point of ammonia depletion unsuited for detection by an algorithm. No air flow algorithms were developed in this experimental work.

- As the control system maintained a fixed dissolved oxygen concentration the profile provided no information apart from the concentration itself. There were no features that correlated to the depletion of biochemical parameters and the profile was of no use for process control purposes.

6.2 RECOMMENDATIONS

The following recommendations can be drawn from this research.

- Further research needs to be undertaken to clarify the reactor volumes required for aerobic denitrification. The nitrification and denitrification rates in aerobic denitrification processes are a function of the reaction kinetics, floc size, floc density, floc structure, rbCOD loading and bulk DO concentration. Because of the complex physical factors the process is still to be modeled accurately (Metcalf and Eddy (2001)).

- The sludge production rates for the aerobic denitrification process need to be clarified. The results suggest the aerobic denitrification process may offer a lower sludge production rate (relative to a separate stage nitrification-denitrification process). There is little reference in the literature as to the sludge production rates for the aerobic denitrification process.

- Further research is required to determine aeration requirements for the aerobic denitrification process (the lack of accurate models mean the aeration requirements are unknown). It is unclear if the aerobic denitrification process offers the potential for savings in aeration costs.
- The optimum dissolved oxygen concentration range for the aerobic denitrification process and the variables involved need to be determined. For example research by Third (2004) suggests the optimum could be influenced by variables such as the biomass concentration and the

release of "reducing power" in terms of the ability to hydrolyze stored carbon polymers.

- The mechanism behind aerobic nitrogen removal (in the absence of soluble carbon) and quantification of the requirements for carbon in the aerobic denitrification process needs to be determined.

- Further research is required to confirm the status of the ORP ammonia elbow. (The implication made by some researchers that the change in ORP is related to changes in oxidative reductive potential resulting from the depletion of ammonia nitrogen is probably misleading-incorrect).

- Further work could be undertaken to determine the alkalinity requirements for the aerobic denitrification process. In this research the aerobic denitrification produced a pH profile of half the magnitude, that is the pH scale had a maximum 0.8 unit and maximum 0.4 unit difference for the nitrification and aerobic denitrification processes respectively. Reduced alkalinity consumption could be used to support the shortened pathway nitrification-denitrification explanation.

APPENDIX A1.1 - TRACK STUDY ONE (TS1) DOSP 4.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 1 follow

Table A1.1-1 Track study data and nitrogen mass balance calculations TS1

TRACK STUDY

Aeration time	[COD]	$[NH_3-N]$ (A)	$[NO_2-N]$ (B)	$[NO_3-N]$ (C)	[TPN] (D)	* – [Sol TN] (A+B+C)	Rate-loss $[NH_3-N]$	Rate-loss [TPN]	* Rate-loss – [Sol TN]
0	125	20	0	4	27	24			
18	49	16	0	6	25	22	0.19	0.11	0.12
45	25	11	0	8	21	19	0.20	0.13	0.11
83	27	4	0	13	19	17	0.20	0.05	0.06
119	19	0	1	16	19	17	0.11	0.00	0.00
	Loss	Loss	Gain	Gain	Loss	Loss			
	106	20	1	12	8	7			
Units	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.17	mg/L.min	
		SE-05	mg/L.min.mg MLSS	
[MLSS]		3390	mg/L	
MLSS change / 24 hours		459	mg/L.day MLSS	
Cycle time		148	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		10		
Del MLSS / cycle		50	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		40	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	20	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	12	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss *	A-(B+C)	7	mg/L.cycle N	
Estimated assimilated N		5	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		2	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.02	mg/L.min N	

*- total soluble nitrogen (less organic N)

The transformation and removal of ammonia appears to be balanced by the production of nitrate and the likely assimilation. The nitrogen mass balance procedure accounted for all but 9% of the systems nitrogen.

*The assimilated nitrogen was calculated as follows, Change in volatile [MLSS] per cycle = 40 mg/L.cycle * 0.12 (ratio of N in biomass) = 4.8 mg/L.cycle (rounded to 5 mg/L.cycle in Table A1.1-1).

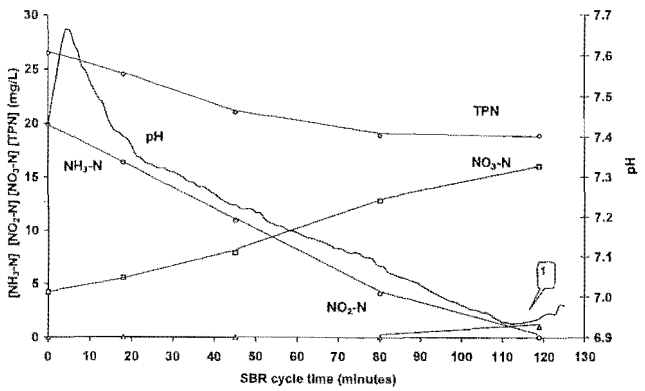


Figure A1.1-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

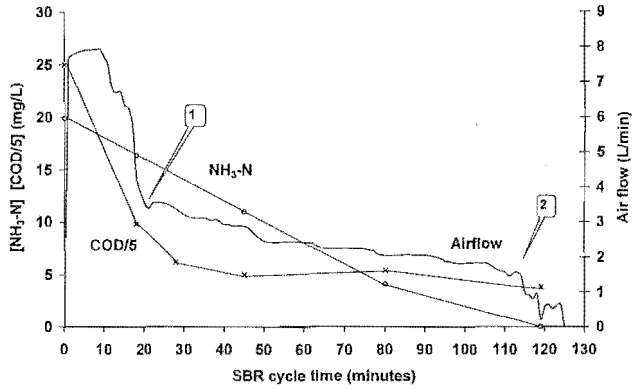


Figure A1.1-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

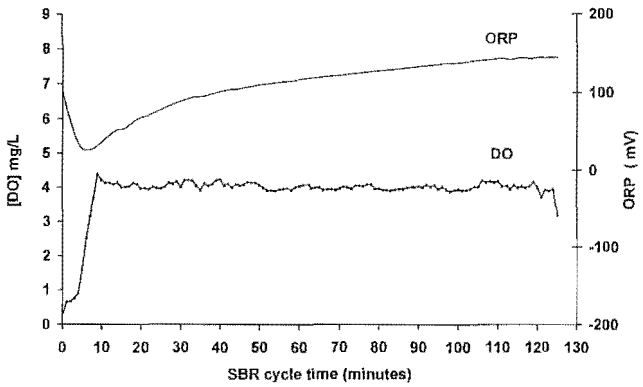


Figure A1.1-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A1.2 - TRACK STUDY TWO (TS2) DOSP 4.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 2 follow

Table A1.2-1 Track study data and nitrogen mass balance calculations TS2

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	175	22	2	5	31	28			
14	26	15	1	10	28	26	0.52	0.21	0.19
37	25	9	1	14	26	24	0.25	0.09	0.06
88	12	6	1	17	26	24	0.08	0.00	0.01
104	24	0	1	23	26	24	0.23	0.04	0.02
	Loss	Loss	Gain	Gain	Loss	Loss			
	151	22	-1	18	6	5			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

Additional COD taken at 10 minutes, result = 51 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.21	mg/L.min
		6E-05	mg/L.min.mg MLSS
[MLSS]		3586	mg/L
MLSS change / 24 hours		528	mg/L day MLSS
Cycle time		134	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		11	
Del MLSS / cycle		49	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		39	mg/L.cycle
Ratio N in $C_5H_7NO_2$		0.12	
Del NH_3-N	A	22	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	-1	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	18	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	5	mg/L.cycle N
Estimated assimilated N		5	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		0	mg/L N ((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.00	mg/L.min N

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance accounted for all the systems nitrogen.

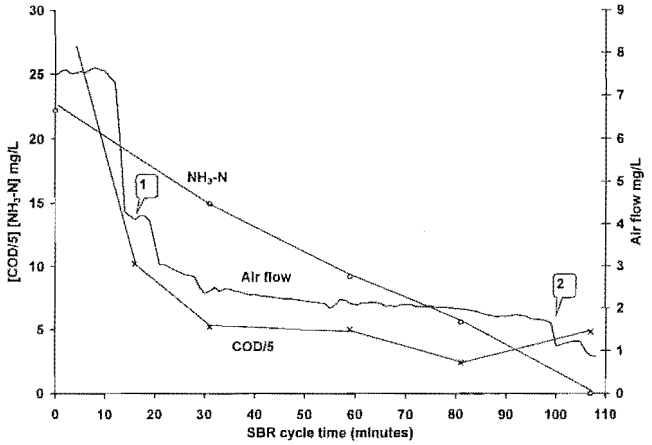


Figure A1.2-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

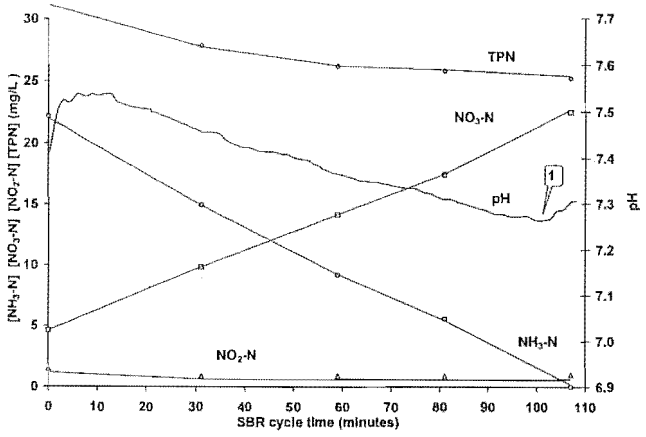


Figure A1.2-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

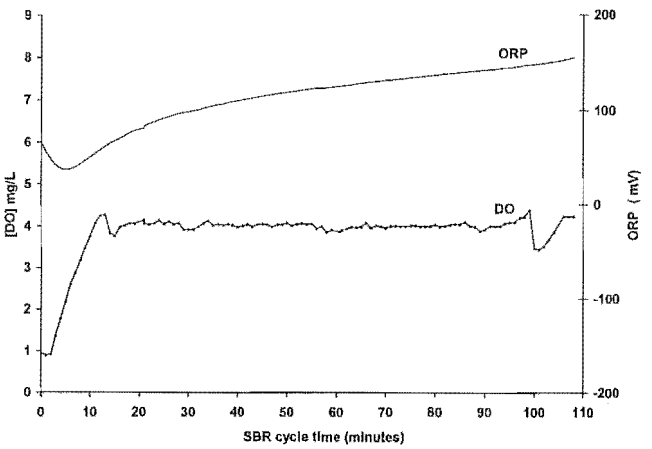


Figure A1.2-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A1.3 - TRACK STUDY THREE (TS3) DOSP 4.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 3 follow

Table A1.3-1 Track study data and nitrogen mass balance calculations TS3

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* - [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss - [Sol TN]
0	161	20	1	5	29	26			
13	71	17	0	6	26	23	0.22	0.23	0.26
36	22	13	0	8	24	21	0.18	0.09	0.07
68	29	9	0	12	23	20	0.14	0.03	0.04
126	26	1	0	19	22	20	0.12	0.02	0.00
144	23	0	0	20	22	20	0.08	0.00	0.02
	Loss	Loss	Gain	Gain	Loss	Loss			
	138	20	-1	15	7	7			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

Additional COD taken at 23 minutes, result = 35 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.14	mg/L.min	
		4E-05	mg/L.min.mg MLSS	
[MLSS]		3115	mg/L	
MLSS change / 24 hours		305	mg/L.day MLSS	
Cycle time		187	minutes	[Aerobic + Settle + 10 minutes fill and decant]
Cycles / day		8		
Del MLSS / cycle		40	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		32	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	20	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	-1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	15	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	7	mg/L.cycle N	
Estimated assimilated N		4	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		3	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.02	mg/L.min N	

*- total soluble nitrogen (less organic N)

The nitrogen mass balance accounted for all but 10% of the systems nitrogen.

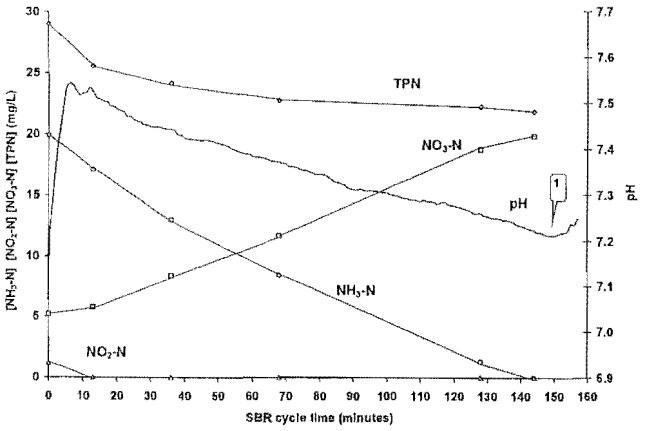


Figure A1.3-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

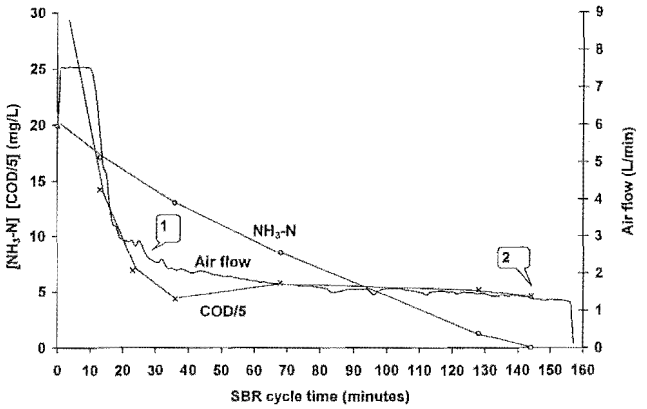


Figure A1.3-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2. Point 2 was present but somewhat unclear.

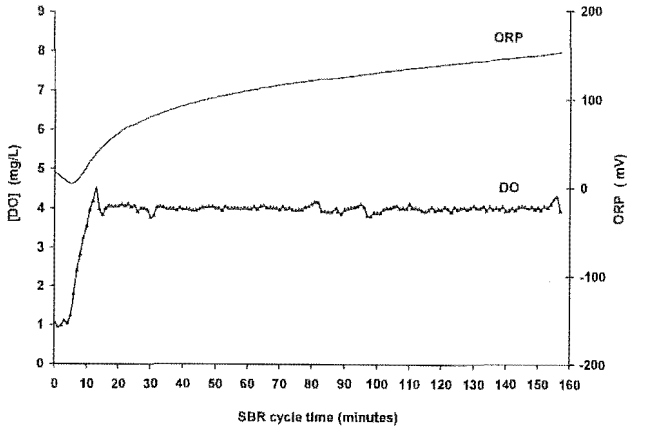


Figure A1.3-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A1.4 - TRACK STUDY FOUR (TS4) DOSP 4.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 4 follow

Table A1.4-1 Track study data and nitrogen mass balance calculations TS4

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	145	19	0	6	29	26			
15	50	17	0	8	28	25	0.14	0.07	0.03
32	29	14	0	10	26	24	0.21	0.12	0.10
54	19	9	0	13	25	22	0.21	0.05	0.08
83	26	4	0	16	23	20	0.18	0.07	0.07
109	22	0	1	20	24	21	0.15	-0.04	-0.04
	Loss 123	Loss 19	Gain 1	Gain 13	Loss 5	Loss 5			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

Additional COD taken at 24 minutes, result = 15 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.18	mg/L.min	
		6E-05	mg/L.min.mg MLSS	
[MLSS]		3074	mg/L	
MLSS change / 24 hours		175	mg/L.day MLSS	
Cycle time		143	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		10		
Del MLSS / cycle		17	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		14	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	19	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	13	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	5	mg/L.cycle N	
Estimated assimilated N		2	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		3	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.03	mg/L.min N	

*~ total soluble nitrogen (less organic N)

With reference to table A1.4-1 the nitrogen mass balance accounted for all but 12% of the systems nitrogen.

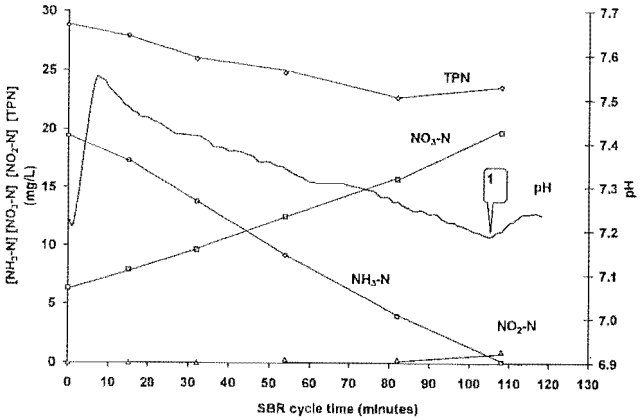


Figure A1.4-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

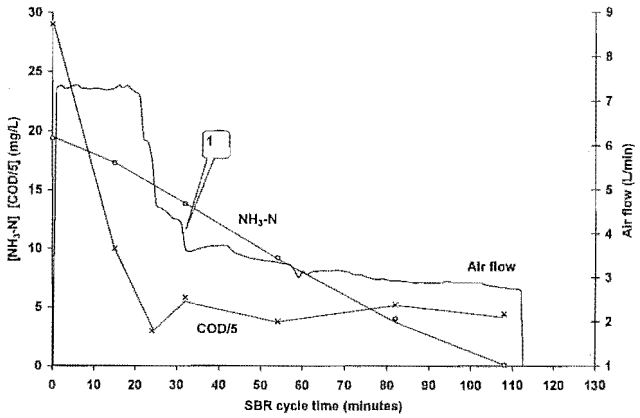


Figure A1.4-2 Air flow rate [ammonia nitrogen], and [COD]

The aeration system struggled in the initial stages of the cycle to reach the target DOSP and it is thought the DO transfer efficiency may have fallen due to problems with the aeration stones. Following this track study the aeration stones were replaced and this appeared to rectify the problem. The air flow rate profile provided an indication of the point of COD depletion point 1. The point of ammonia depletion was not clearly visible.

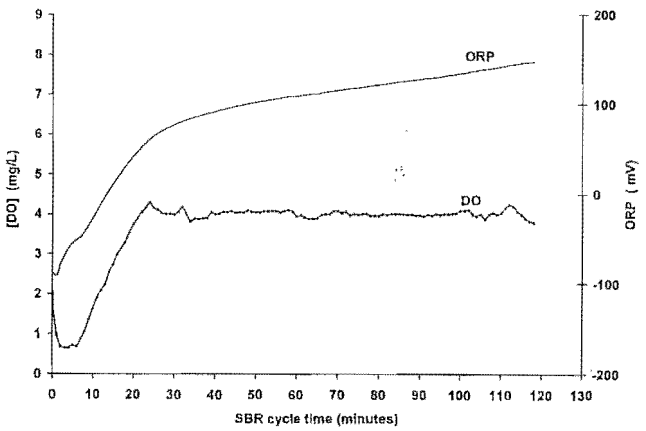


Figure A1.4-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A1.5 - TRACK STUDY FIVE (TS5) DOSP 4.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 5 follow

Table A1.5-1 Track study data and nitrogen mass balance calculations TS5

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	159	21	1	5	30	28			
14	42	18	1	8	28	26	0.21	0.14	0.14
37	24	13	0	11	27	25	0.20	0.07	0.00
97	26	3	0	21	26	24	0.18	0.01	0.01
125	21	0	0	24	26	24	0.09	0.01	0.00
	Loss	Loss	Gain	Gain	Loss	Loss			
	138	21	-1	17	4	4			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.16	mg/L.min	
		6E-05	mg/L.min.mg MLSS	
[MLSS]		2972	mg/L	
MLSS change / 24 hours		115	mg/L.day MLSS	
Cycle time		147	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		10		
Del MLSS / cycle		12	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		9	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	21	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	-1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	17	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A+(B+C)	4	mg/L.cycle N	
Estimated assimilated N		1	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		3	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.02	mg/L.min N	

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance accounted for all but 11% of the systems nitrogen.

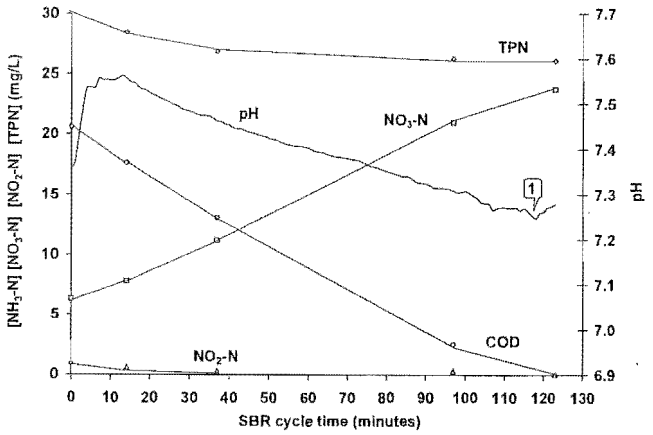


Figure A1.5-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

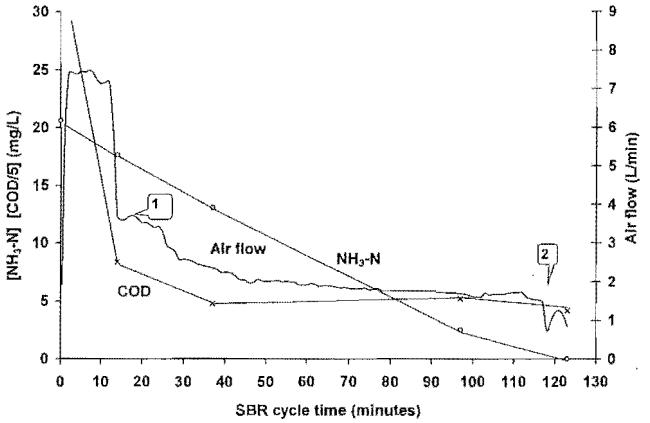


Figure A1.5-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

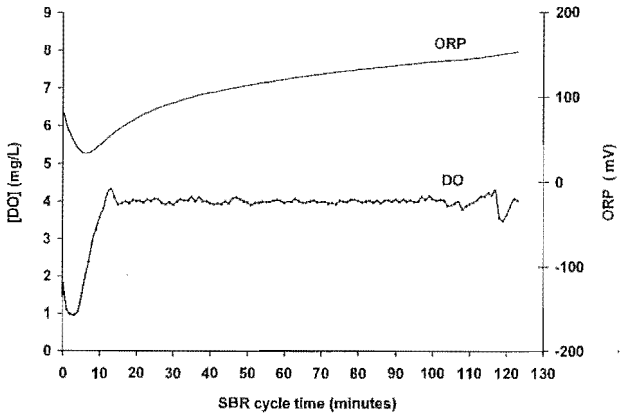


Figure A1.5-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A1.6 - TRACK STUDY SIX (TS6) DOSP 4.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 6 follow

Table A1.6-1 Track study data and nitrogen mass balance calculations TS6

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	152	20	1	5	29	28			
20	31	17	0	6	26	26	0.21	0.14	0.14
47	26	12	0	8	24	25	0.20	0.07	0.06
82	23	6	1	12	24	24	0.18	0.01	0.01
143	22	0	1	18	22	24	0.09	0.01	0.00
	Loss	Loss	Gain	Gain	Loss	Loss			
	130	20	0	13	7	4			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.14	mg/L.min	
		4.E-05	mg/L.min.mg MLSS	
[MLSS]		3639	mg/L	
MLSS change / 24 hours		544	mg/L.day MLSS	
Cycle time		165	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		8		
Del MLSS / cycle		62	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		50	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	20	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	0	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	13	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	7	mg/L.cycle N	
Estimated assimilated N		6	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		1	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.01	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance accounted for all but 3% of the systems nitrogen.

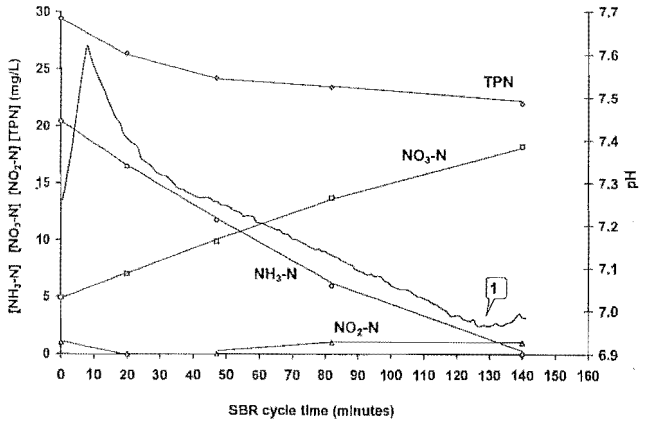


Figure A1.6-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

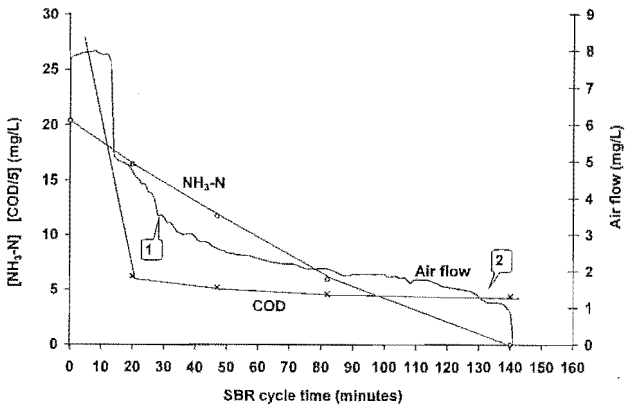


Figure A1.6-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

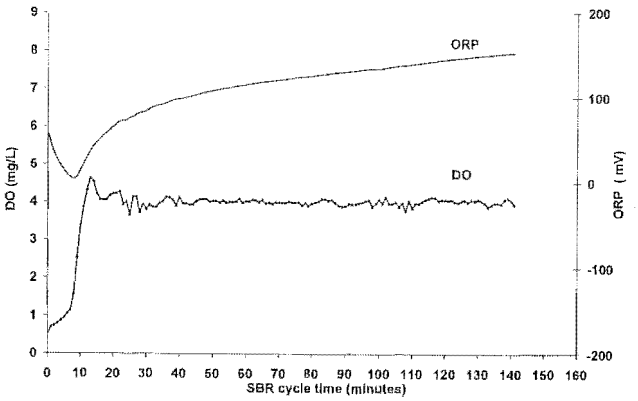


Figure A1.6-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A1.7 - TRACK STUDY SEVEN (TS7) DOSP 4.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 7 follow

Table A1.7-1 Track study data and nitrogen mass balance calculations TS7

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	161	19	0	8	30	28			
17	45	16	0	10	29	26	0.2	0.1	0.1
39	24	12	0	13	28	25	0.2	0.1	0.1
69	25	6	0	17	25	24	0.2	0.0	0.0
97	19	0	1	21	25	24	0.1	0.0	0.0
	Loss	Loss	Gain	Gain	Loss	Loss			
	142	19	1	13	5	4			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.19	mg/L.min	
		6E-05	mg/L.min.mg MLSS	
[MLSS]		3179	mg/L	
MLSS change / 24 hours		381	mg/L.day MLSS	
Cycle time		146	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		10		
Del MLSS / cycle		38	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		31	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	19	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	13	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A+(B+C)	5	mg/L.cycle N	
Estimated assimilated N		4	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		1	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.01	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance accounted for all but 3% of the systems nitrogen.

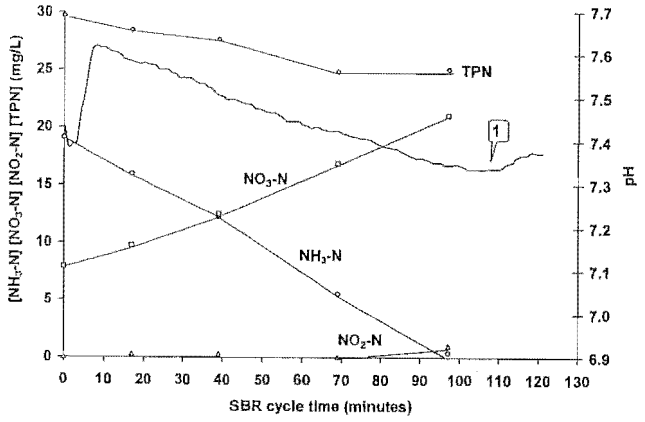


Figure A1.7-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

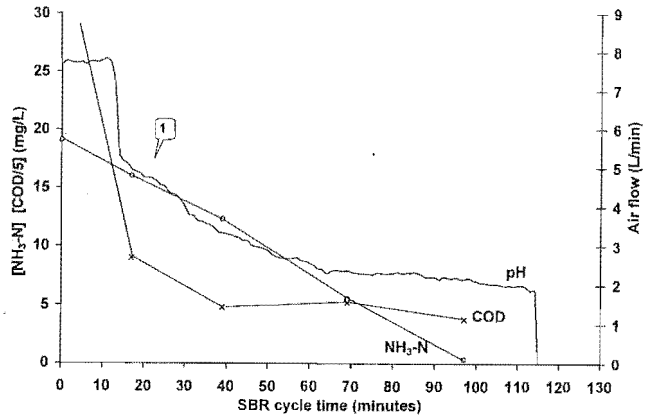


Figure A1.7-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1. There was no clear indication of the point of ammonia depletion.

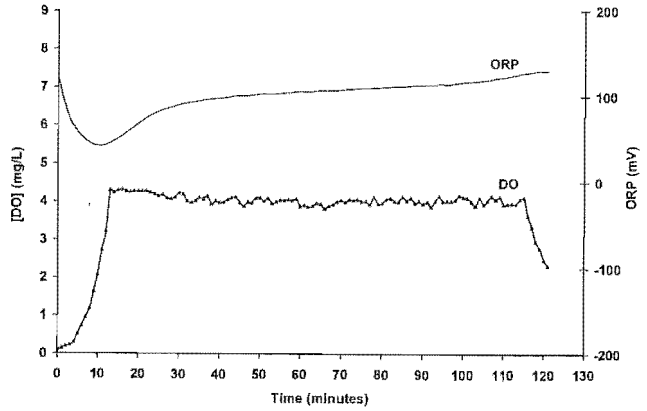


Figure A1.7-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A2.1 - TRACK STUDY ONE (TS1) DOSP 2.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 1 follow

Table A2.1-1 Track study data and nitrogen mass balance calculations TS1

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	149	19	2	5	29	26			
46	34	13	1	10	26	24	0.13	0.05	0.04
81	24	7	1	14	26	23	0.18	0.03	0.03
120	20	1	0	18	23	20	0.16	0.07	0.08
149	15	0	1	20	24	21	0.03	-0.04	-0.04
	Loss	Loss	Loss	Gain	Loss	Loss			
	130	18	1	15	5	5			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

*Additional COD taken at 15 minutes, result = 49 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.12	mg/L.min	
		5E-05	mg/L.min.mg MLSS	
[MLSS]		2504	mg/L	
MLSS change / 24 hours		104	mg/L.day MLSS	
Cycle time		170	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		8		
Del MLSS / cycle		12	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		10	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	18	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	15	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	3	mg/L.cycle N	
Estimated assimilated N		1	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		1	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.01	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 11% of the systems nitrogen.

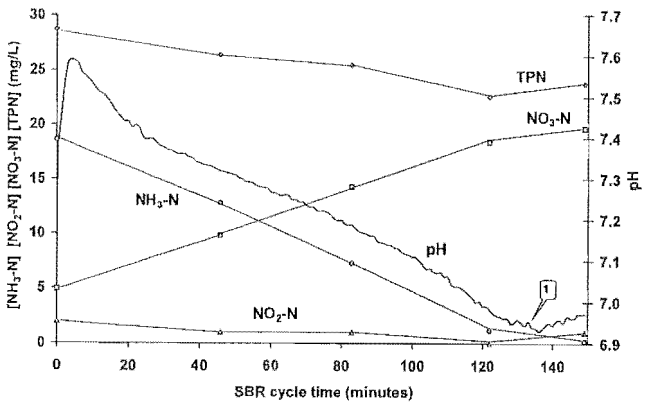


Figure A2.1-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

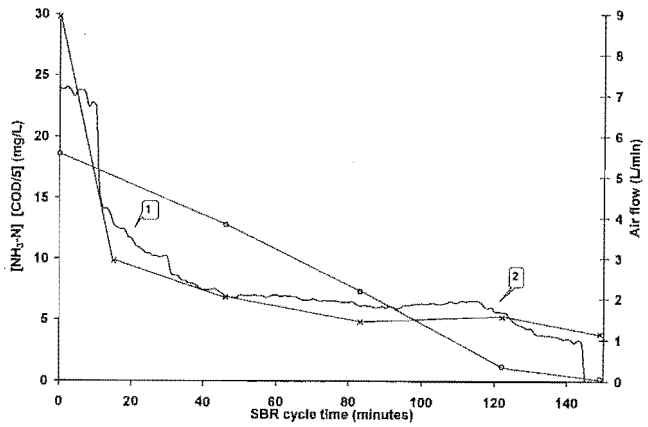


Figure A2.1-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

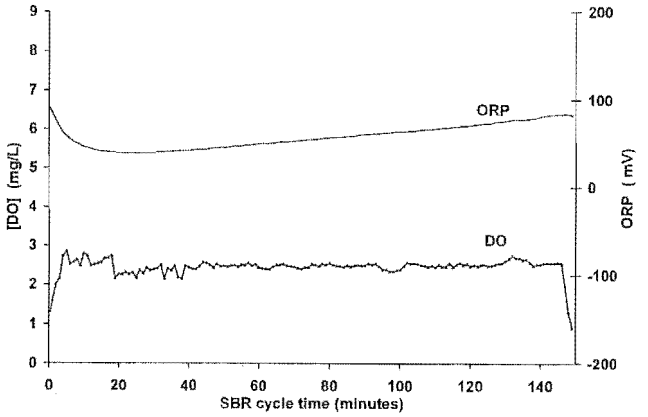


Figure A2.1-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A2.2 - TRACK STUDY TWO (TS2) DOSP 2.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 2 follow

Table A2.2-1 Track study data and nitrogen mass balance calculations TS2

TRACK STUDY

Aeration time	[COD]	[NH3-N] (A)	[NO2-N] (B)	[NO3-N] (C)	[TPN] (D)	* ~ (Sol TN) (A+B+C)	Rate-loss [NH3-N]	Rate-loss [TPN]	* Rate-loss ~ (Sol TN)
0	160	21	1	6	31	26			
32	50	16	1	8	29	23	0.2	0.2	0.3
67	34	14	1	10	27	21	0.2	0.1	0.1
88	25	10	0	11	24	20	0.1	0.0	0.0
114	26	7	0	14	24	20	0.1	0.0	0.0
185	19	1	1	18	23	20	0.1	0.0	0.0
	Loss	Loss	Gain	Gain	Loss	Loss			
	161	20	0	13	8	6			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.12	mg/L.min	
		4E-05	mg/L.min.mg MLSS	
[MLSS]		2901	mg/L	
MLSS change / 24 hours		200	mg/L.day MLSS	
Cycle time		207	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		7		
Del MLSS / cycle		29	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		23	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	20	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_3-N	B	0	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_2-N	C	13	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	8	mg/L.cycle N	
Estimated assimilated N		3	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		5	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.03	mg/L.min N	

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 14% of the systems nitrogen.

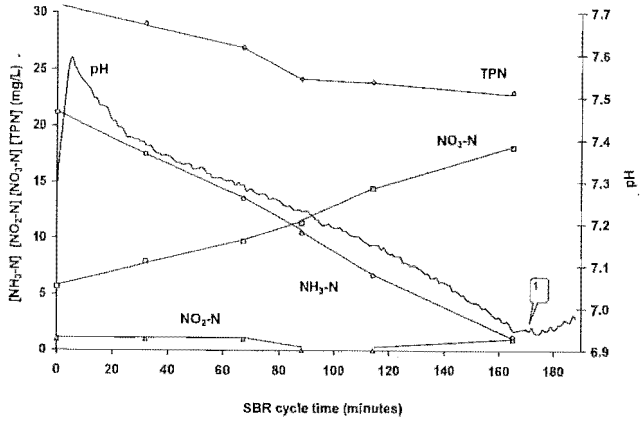


Figure A2.2-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

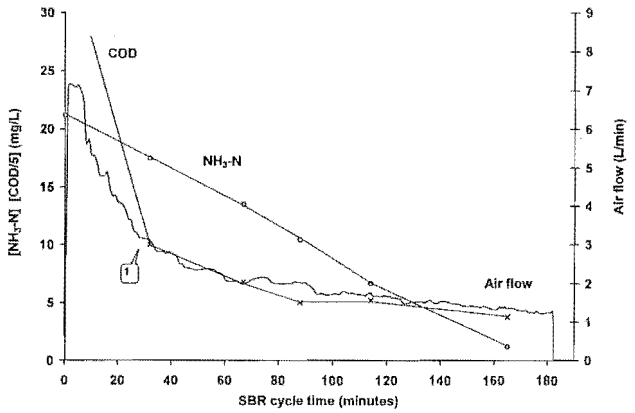


Figure A2.2-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

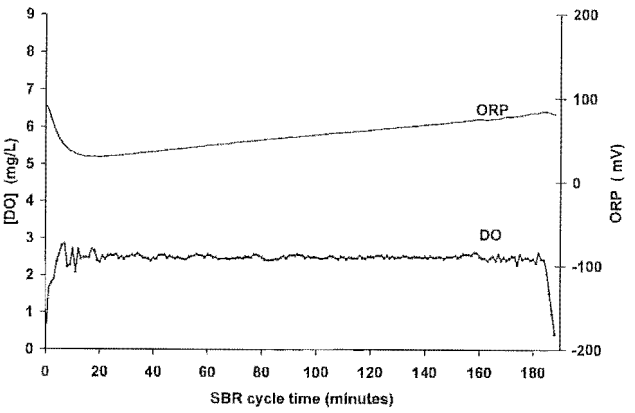


Figure A2.2-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A2.3 - TRACK STUDY THREE (TS3) DOSP 2.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 3 follow

Table A2.3-1 Track study data and nitrogen mass balance calculations TS3

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	147	20	0	5	28	25			
21	50	17	0	7	27	24	0.13	0.04	0.03
52	41	12	1	9	25	22	0.16	0.09	0.08
90	22	8	0	14	25	22	0.10	0.00	0.01
132	28	2	1	16	25	22	0.14	0.00	0.00
	Loss	Loss	Gain	Gain	Loss	Loss			
	119	17	1	13	3	3			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.132	mg/L.min
		4E-05	mg/L.min.mg MLSS
[MLSS]		3620	mg/L
MLSS change / 24 hours		152	mg/L.day MLSS
Cycle time		191	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		6	
Del MLSS / cycle		20	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		16	mg/L.cycle
Ratio N in $C_5H_7NO_2$		0.12	
Del NH_3-N	A	17	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	1	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	13	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	3	mg/L.cycle N
Estimated assimilated N		2	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		1	mg/L N ((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.01	mg/L.min N

*~ (total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 4% of the systems nitrogen.

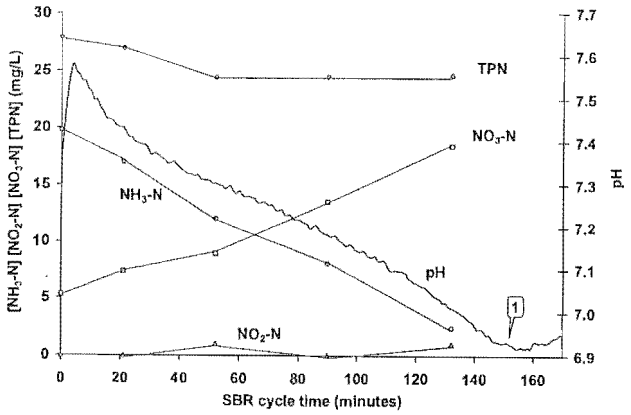


Figure A2.3-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase. Note the test samples taken at 160 minutes were lost due to an experimental error however points indicate the ammonia valley occurred at the point of ammonia depletion.

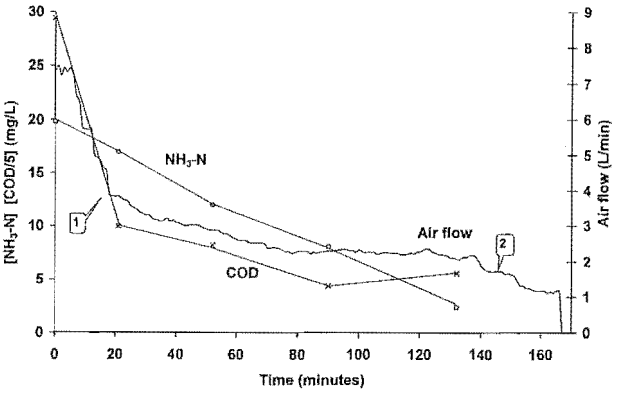


Figure A2.3-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

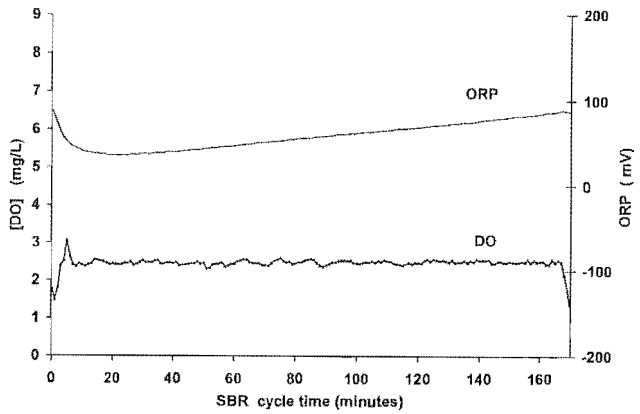


Figure A2.3-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A2.4 - TRACK STUDY FOUR (TS4) DOSP 2.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 4 follow

Table A2.4-1 Track study data and nitrogen mass balance calculations TS4

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	121	18	0	2	23	20			
40	36	11	1	6	21	18	0.19	0.06	0.05
80	25	8	0	6	19	16	0.13	0.11	0.12
89	23	5	0	12	19	16	0.11	-0.02	-0.02
117	12	0	1	16	19	17	0.17	0.02	-0.02
	Loss	Loss	Gain	Gain	Loss	Loss			
	109	18	1	14	4	3			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

*Additional COD taken at 24 minutes, result = 35 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.156	mg/L.min	
		4E-05	mg/L.min.mg MLSS	
[MLSS]		3944	mg/L	
MLSS change / 24 hours		302	mg/L.day MLSS	
Cycle time		145	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		10		
Del MLSS / cycle		30	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		24	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	18	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	14	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	3	mg/L.cycle N	
Estimated assimilated N		3	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		0	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.00	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 1% of the systems nitrogen.

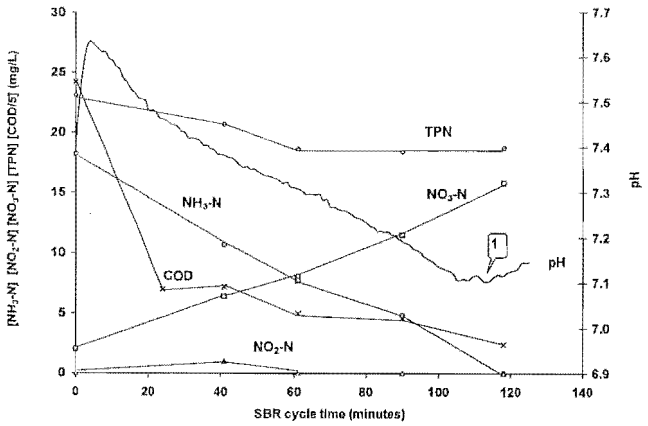


Figure A2.4-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase. There was a problem with the logging of the air flow rate and data was not obtained for this track study. As the air flow rate profile was not available the [COD] data was included on the pH profile.

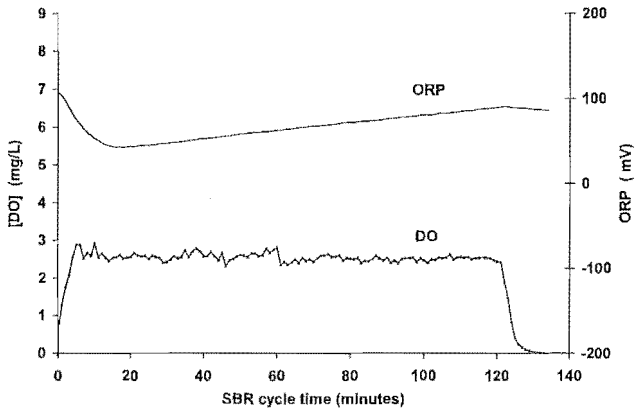


Figure A2.4-2 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A2.5 - TRACK STUDY FIVE (TS5) DOSP 2.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 5 follow

Table A2.5-1 Track study data and nitrogen mass balance calculations TS4

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* - [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss - [Sol TN]
0	128	19	0	8	27	24			
34	31	13	0	8	24	21	0.17	0.09	0.09
59	31	10	0	11	24	21	0.12	-0.01	0.00
93	16	5	0	14	21	18	0.15	0.10	0.09
125	19	0	1	17	21	19	0.13	-0.01	-0.01
	Loss	Loss	Gain	Gain	Loss	Loss			
	109	18	1	12	6	6			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

*Additional COD taken at 16 minutes, result = 45 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.14	mg/L.min	
		5E-05	mg/L.min.mg MLSS	
[MLSS]		2834	mg/L	
MLSS change / 24 hours		266	mg/L.day MLSS	
Cycle time		152	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		9		
Del MLSS / cycle		28	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		22	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	18	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	12	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	6	mg/L.cycle N	
Estimated assimilated N		3	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		3	mg/L N	((+) = loss of N (-) = Gain of N)
Rate Unaccounted N loss		0.02	mg/L.min N	

*- total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 10% of the systems nitrogen.

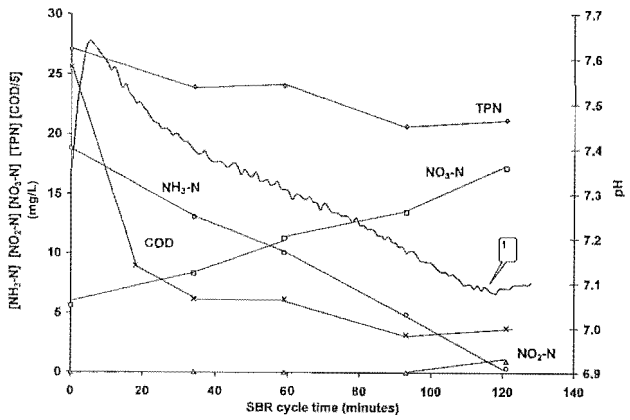


Figure A2.5-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase. There was a problem with the logging of the air flow rate and data was not obtained for this track study. As the air flow rate profile was not available the [COD] data was included on the pH profile.

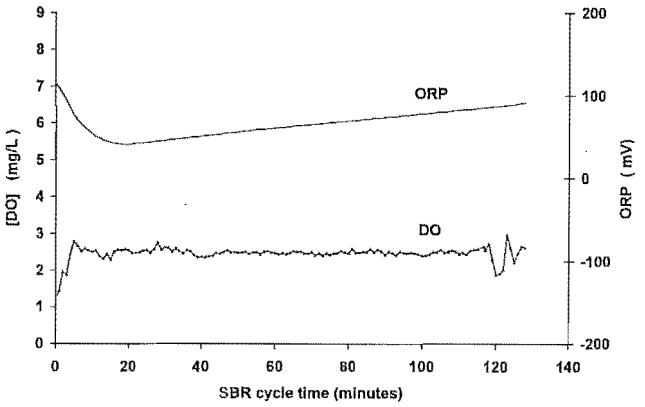


Figure A2.5-2 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A2.6 - TRACK STUDY SIX (TS6) DOSP 2.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 6 follow

Table A2.6-1 Track study data and nitrogen mass balance calculations TS6

TRACK STUDY

Aeration time	[COD]	$[NH_3\text{-}N]$ (A)	$(NO_2\text{-}N)$ (B)	$[NO_3\text{-}N]$ (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss $(NH_3\text{-}N)$	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	115	16	1	4	23	20			
33	31	12	0	6	21	18	0.11	0.07	0.07
56	19	9	0	8	19	17	0.13	0.07	0.06
91	24	4	1	10	17	15	0.15	0.05	0.06
121	22	1	1	12	16	13	0.10	0.04	0.05
	Loss	Loss	Gain	Gain	Loss	Loss			
	93	15	0	8	7	7			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

*Additional COD taken at 15 minutes, result = 46 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.12	mg/L.min	
		4E-05	mg/L.min.mg MLSS	
[MLSS]		3194	mg/L	
MLSS change / 24 hours		309	mg/L.day MLSS	
Cycle time		153	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		9		
Del MLSS / cycle		33	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		26	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	15	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	0	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	8	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	7	mg/L.cycle N	
Estimated assimilated N		3	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		4	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.03	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 16% of the systems nitrogen.

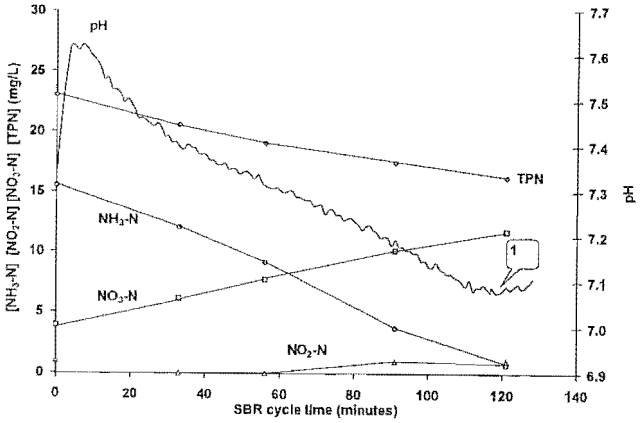


Figure A2.6-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

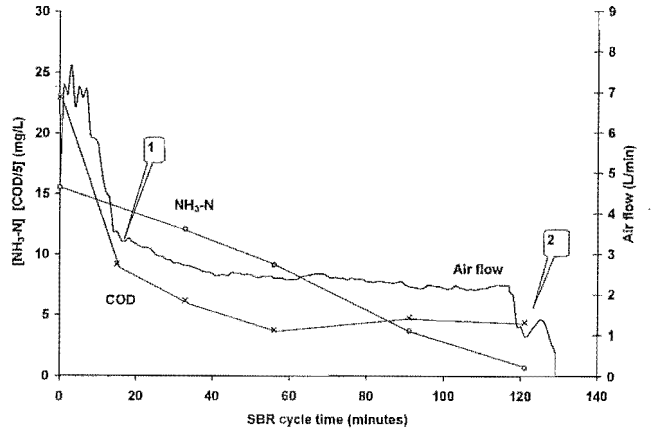


Figure A2.6-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

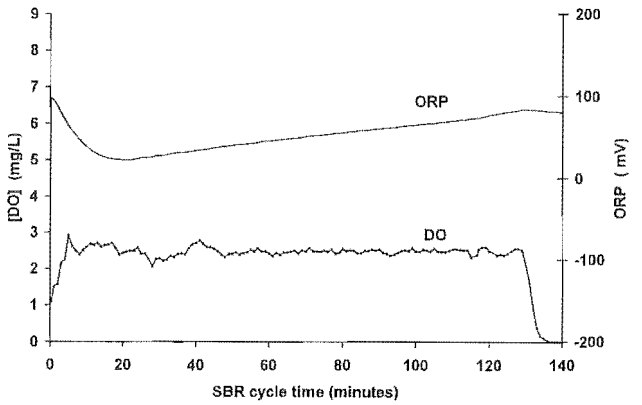


Figure A2.6-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A2.7 - TRACK STUDY SEVEN (TS7) DOSP 2.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 7 follow

Table A2.7-1 Track study data and nitrogen mass balance calculations TS6

TRACK STUDY

Aeration time	[COD]	[NH3-N] (A)	[NO2-N] (B)	[NO3-N] (C)	[TPN] (D)	* ~ (Sol TN) (A+B+C)	Rate-loss [NH3-N]	Rate-loss [TPN]	* Rate-loss ~ (Sol TN)
0	170	20	0	4	27	24			
20	49	18	1	5	26	24	0.07	0.02	0.00
63	26	14	1	6	23	21	0.14	0.09	0.11
98	29	8	0	9	22	18	0.18	0.03	0.09
132	20	4	1	11	20	16	0.14	0.05	0.05
169	19	1	0	15	19	16	0.10	0.07	0.00
		Loss	Loss	Gain	Gain	Loss	Loss		
		151	19	0	11	8	8		
Minutes		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.12	mg/L.min	
		3E-05	mg/L.min.mg MLSS	
[MLSS]		3594	mg/L	
MLSS change / 24 hours		343	mg/L.day MLSS	
Cycle time		206	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		7		
Del MLSS / cycle		49	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		39	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	19	mg/L cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	0	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	11	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	8	mg/L.cycle N	
Estimated assimilated N		5	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		3	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.02	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 11% of the systems nitrogen.

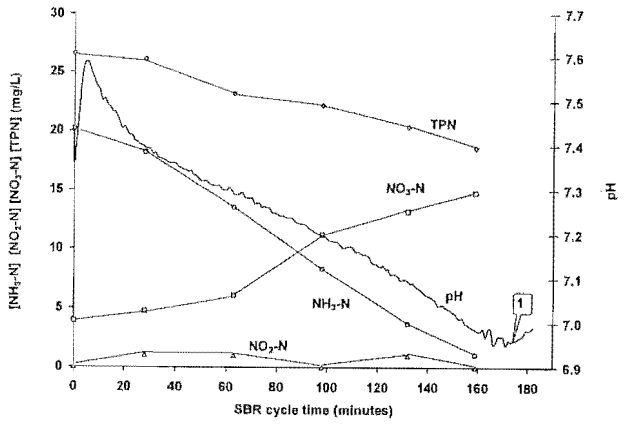


Figure A2.7-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

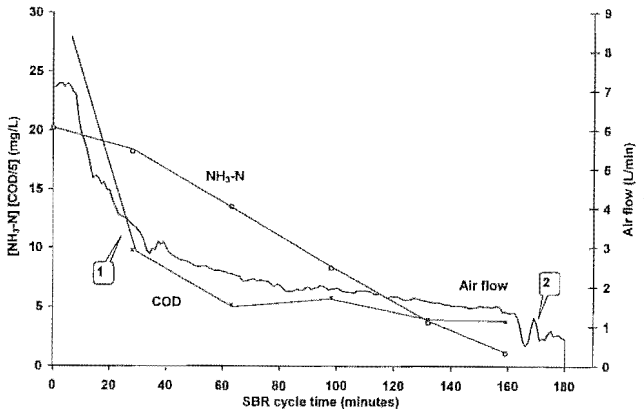


Figure A2.7-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

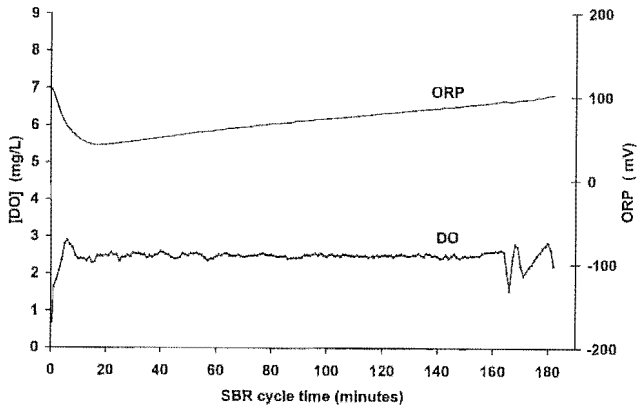


Figure A2.7-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A3.1 - TRACK STUDY ONE (TS1) DOSP 1.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 1 follow

Table A3.1-1 Track study data and nitrogen mass balance calculations TS1

TRACK STUDY

Aeration Time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* - [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss - [Sol TN]
0	130	20	3	3	28	26			
37	35	16	3	4	25	23	0.11	0.09	0.09
92	20	11	5	5	24	21	0.09	0.02	0.04
144	23	7	5	8	21	20	0.07	0.05	0.01
232	18	0	6	10	18	16	0.08	0.03	0.05
	Loss	Loss	Gain	Gain	Loss	Loss			
	112	19	3	6	10	10			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.08	mg/L.min
		3E-05	mg/L.min.mg MLSS
[MLSS]		2912	mg/L
MLSS change / 24 hours		111	mg/L.day MLSS
Cycle time		264	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		5	
Del MLSS / cycle		20	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		16	mg/L.cycle
Ratio N in $C_5H_7NO_2$		0.12	
Del NH_3-N	A	19	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	3	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	6	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	10	mg/L.cycle N
Estimated assimilated N		2	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		8	mg/L N ((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.09	mg/L.min N

*- total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 27% of the systems nitrogen.

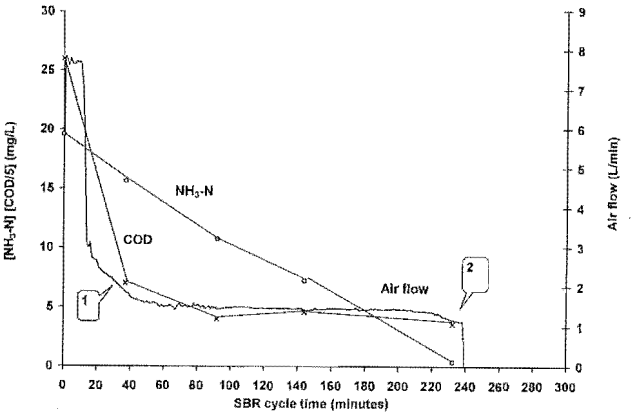


Figure A3.1-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

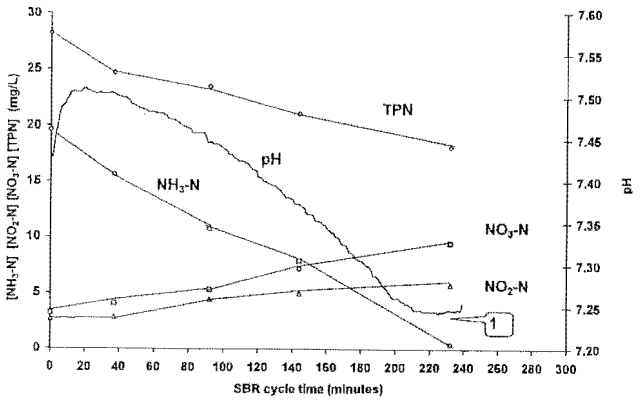


Figure A3.1-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

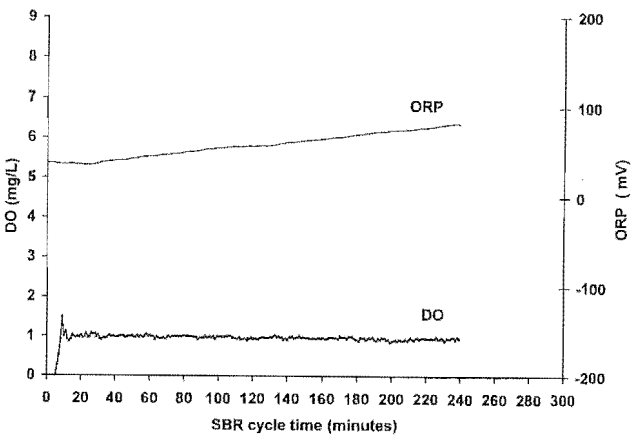


Figure A3.1-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A3.2 - TRACK STUDY TWO (TS2) DOSP 1.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 2 follow

Table A3.2-1 Track study data and nitrogen mass balance calculations TS2

TRACK STUDY

Aeration time	[COD]	$[NH_3\text{-}N]$ (A)	$[NO_2\text{-}N]$ (B)	$[NO_3\text{-}N]$ (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss $[NH_3\text{-}N]$	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	130	20	3	3	28	26			
37	35	16	3	4	25	23	0.11	0.09	0.08
92	20	11	5	5	24	21	0.09	0.02	0.04
144	23	7	5	8	21	20	0.07	0.05	0.01
232	18	0	6	10	18	16	0.08	0.03	0.05
	Loss	Loss	Gain	Gain	Loss	Loss			
	112	18	3	6	10	10			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.06	mg/L.min	
		3E-05	mg/L.min.mg MLSS	
[MLSS]		2912	mg/L	
MLSS change / 24 hours		111	mg/L.day MLSS	
Cycle time		264	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		5		
Del MLSS / cycle		20	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		16	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	19	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	3	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	8	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	10	mg/L.cycle N	
Estimated assimilated N		2	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		8	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.03	mg/L.min N	

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 35% of the systems nitrogen.

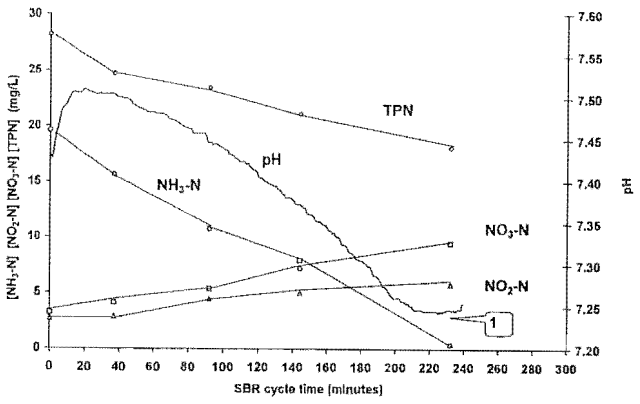


Figure A3.2-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

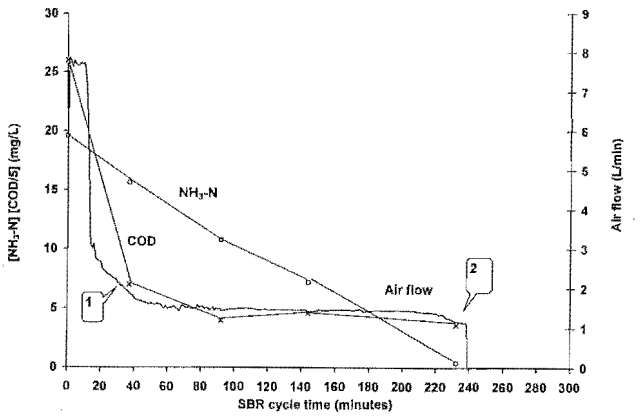


Figure A3.2-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2. The point of ammonia depletion was slight.

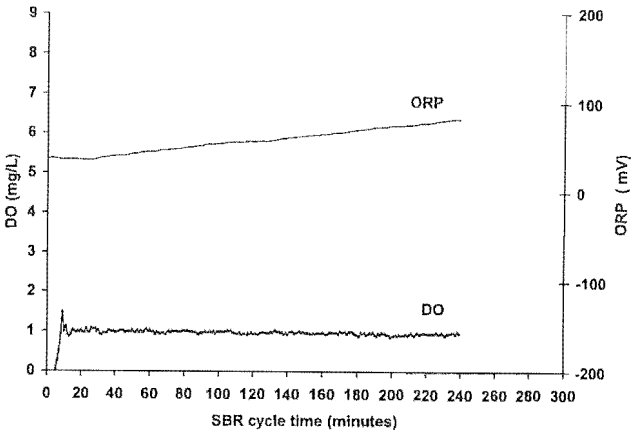


Figure A3.2-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A3.3 - TRACK STUDY THREE (TS3) DOSP 1.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 3 follow

Table A3.3-1 Track study data and nitrogen mass balance calculations TS3

TRACK STUDY

Aeration time	[COD]	$[NH_3-N]$ (A)	$[NO_2-N]$ (B)	$[NO_3-N]$ (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss $[NH_3-N]$	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	144	16	2	3	26	23			
49	35	14	2	6	23	22	0.08	0.06	0.03
108	26	11	3	4	20	18	0.05	0.05	0.07
181	22	3	4	7	16	13	0.11	0.06	0.06
241	24	0	5	7	15	12	0.04	0.02	0.02
	Loss	Loss	Gain	Gain	Loss	Loss			
	120	16	3	4	12	11			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

Additional COD taken at 23 minutes, result = 45 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.07	mg/L.min	
		2E-05	mg/L.min.mg MLSS	
(MLSS)		3105	mg/L	
MLSS change / 24 hours		96	mg/L.day MLSS	
Cycle time		277	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		5		
Del MLSS / cycle		18	mg/L.cycle	
VSS/TSS		0.60		
Del MLSS Volatile		15	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	16	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	3	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	4	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	11	mg/L.cycle N	
Estimated assimilated N		2	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		9	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.04	mg/L.min N	

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 37% of the systems nitrogen.

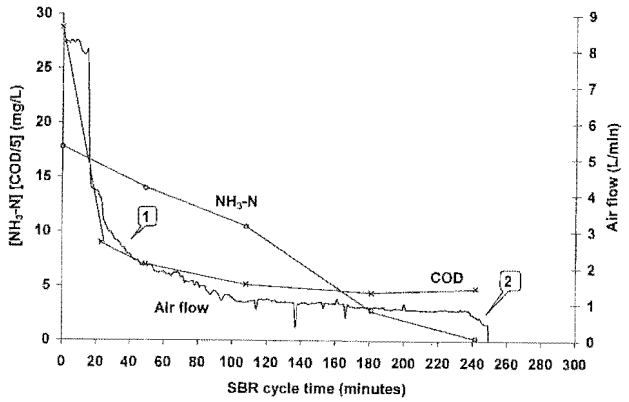


Figure A3.3-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

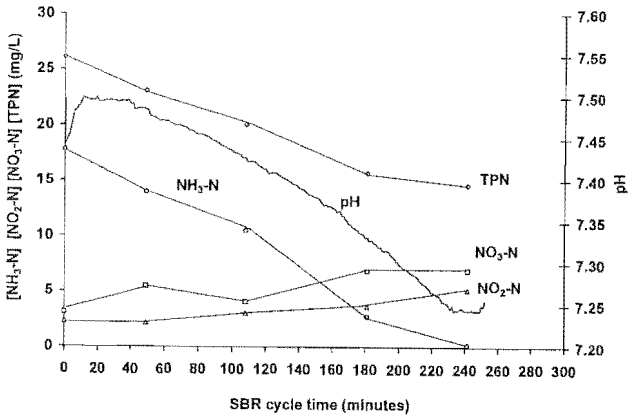


Figure A3.3-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

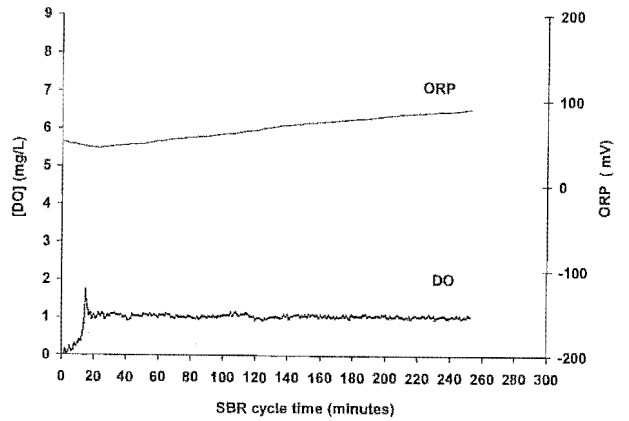


Figure A3.3-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A3.4 - TRACK STUDY FOUR (TS4) DOSP 1.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 4 follow

Table A3.4-1 Track study data and nitrogen mass balance calculations TS4

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	189	20	3	5	31	28			
53	39	15	3	7	28	25	0.09	0.04	0.05
133	21	10	5	7	24	22	0.07	0.06	0.04
205	21	4	6	10	21	19	0.09	0.03	0.04
257	26	0	6	11	20	17	0.07	0.03	0.03
	Loss	Loss	Gain	Gain	Loss	Loss			
	143	20	4	6	11	11			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.08	mg/L.min
		2E-05	mg/L.min.mg MLSS
[MLSS]		3489	mg/L
MLSS change / 24 hours		106	mg/L.day MLSS
Cycle time		299	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		5	
Del MLSS / cycle		22	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		18	mg/L.cycle
Ratio N to $C_5H_7NO_2$		0.12	
Del NH_3-N	A	29.4	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	3.6	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	6.1	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	19.7	mg/L.cycle N
Estimated assimilated N		2.2	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		8.5	mg/L N ((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.03	mg/L.min N

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 28% of the systems nitrogen.

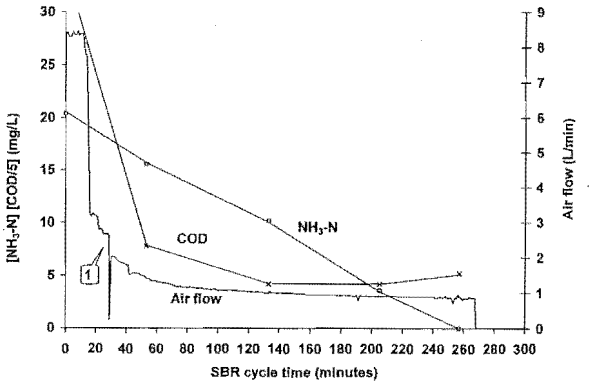


Figure A3.4-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

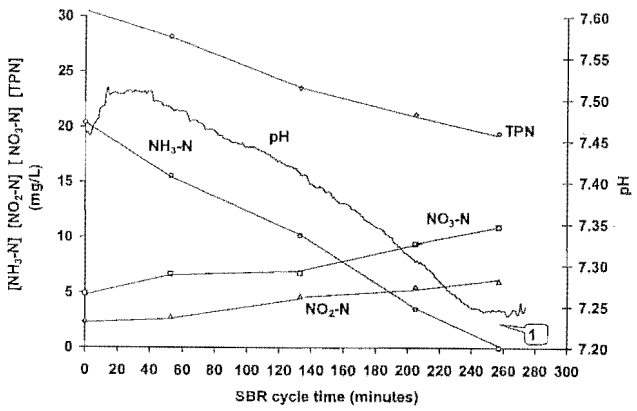


Figure A3.4-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

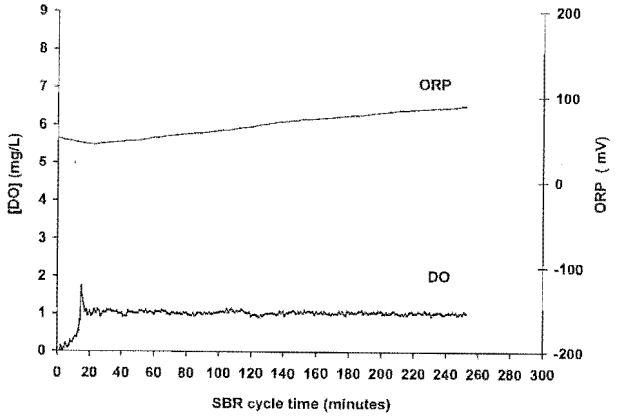


Figure A3.4-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A3.5 - TRACK STUDY FIVE (TS5) DOSP 1.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 5 follow

Table A3.5-1 Track study data and nitrogen mass balance calculations TS5

TRACK STUDY

Aeration time	[COD]	$[NH_3-N]$ (A)	$[NO_2-N]$ (B)	$[NO_3-N]$ (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss $[NH_3-N]$	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	180	21	2	4	29	26			
34	40	19	1	4	27	25	0.05	0.05	0.04
103	20	11	2	6	23	19	0.12	0.06	0.08
169	23	6	3	7	19	17	0.06	0.07	0.03
246	23	1	4	10	17	15	0.08	0.03	0.03
	Loss	Loss	Gain	Gain	Loss	Loss			
	157	20	3	6	12	11			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

*Additional COD taken at 47 minutes, result = 28 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.08	mg/L.min	
		3E-05	mg/L.min.mg MLSS	
[MLSS]		3012	mg/L	
MLSS change / 24 hours		258	mg/L day MLSS	
Cycle time		289	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		5		
Del MLSS / cycle		52	mg/L cycle	
VSS/TSS		0.80		
Del MLSS Volatile		41	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	20	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	3	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	6	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	11	mg/L.cycle N	
Estimated assimilated N		5	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		6	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.05	mg/L.min N	

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 22% of the systems nitrogen.

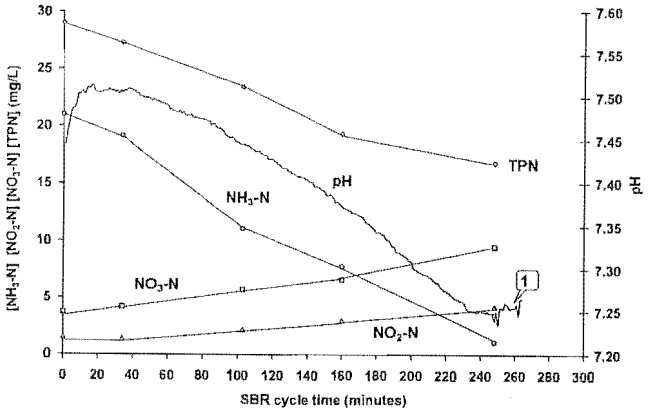


Figure A3.5-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

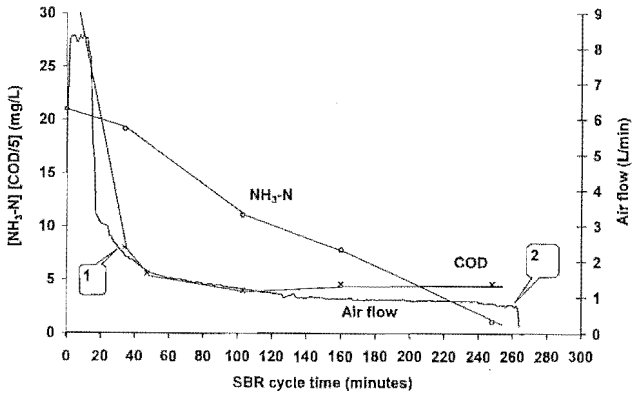


Figure A3.5-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

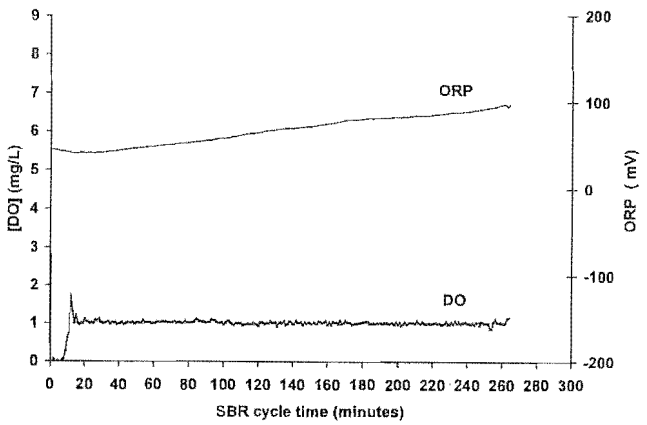


Figure A3.5-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A3.6 - TRACK STUDY SIX (TS6) DOSP 1.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 6 follow

Table A3.6-1 Track study data and nitrogen mass balance calculations TS6

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* – [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss – [Sol TN]
0	161	19	2	2	26	23			
35	45	17	2	3	25	22	0.07	0.04	0.03
78	28	12	2	5	23	20	0.10	0.05	0.05
151	19	7	3	7	19	17	0.07	0.05	0.04
232	23	1	5	10	18	15	0.08	0.02	0.02
	Loss	Loss	Gain	Gain	Loss	Loss			
	138	18	3	8	8	8			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification	9.08	mg/L.min	
	2E-05	mg/L.min.mg MLSS	
[MLSS]	3507	mg/L	
MLSS change / 24 hours	212	mg/L.day MLSS	
Cycle time	278	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day	5		
Del MLSS / cycle	41	mg/L.cycle	
VSS/TSS	0.80		
Del MLSS Volatile	33	mg/L.cycle	
Ratio N to $C_5H_7NO_2$	0.12		
Del NH_3-N A	18	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N B	3	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N C	8	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss A-(B+C)	8	mg/L.cycle N	
Estimated assimilated N	4	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss	3	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss	0.01	mg/L.min N	

* – total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 12% of the systems nitrogen.

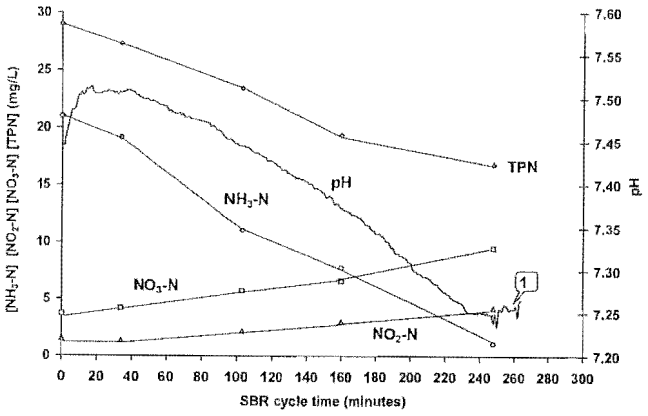


Figure A3.6-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

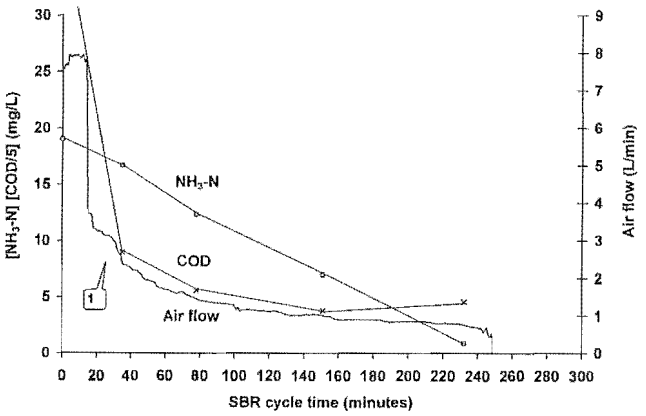


Figure A3.6-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

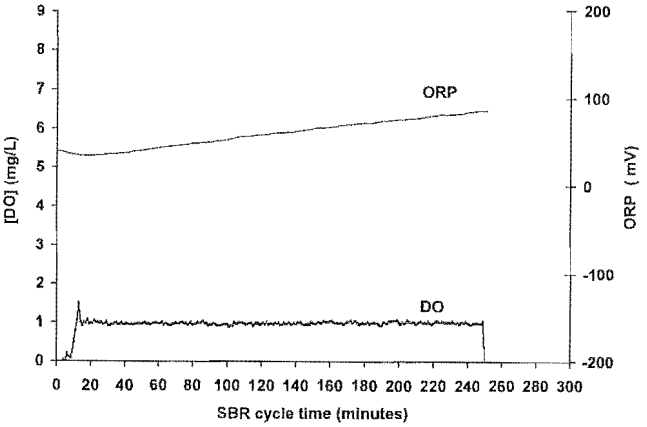


Figure A3.6-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A3.7 - TRACK STUDY SEVEN (TS7) DOSP 1.0

The biochemical data, nitrogen mass balance calculations, and online data for track study 7 follow

Table A3.7-1 Track study data and nitrogen mass balance calculations TS7

TRACK STUDY

Aeration time	[COD]	$[NH_3-N]$ (A)	$[NO_2-N]$ (B)	$[NO_3-N]$ (C)	[TPN] (D)	* – [Sol TN] (A+B+C)	Rate-loss $[NH_3-N]$	Rate-loss [TPN]	* Rate-loss – [Sol TN]
0	155	18	2	4	27	24			
66	19	13	3	5	24	21	0.07	0.04	0.04
122	22	11	3	6	22	19	0.05	0.03	0.04
198	18	5	6	7	20	18	0.07	0.03	0.02
257	20	1	6	8	19	16	0.07	0.02	0.03
	Loss	Loss	Gain	Gain	Less	Loss			
	135	17	4	5	8	8			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

*Additional COD taken at 21 minutes, result = 28 mg/L

NITROGEN MASS BALANCE

Average rate nitrification		0.07	mg/L.min
		2E-05	mg/L.min.mg MLSS
[MLSS]		3793	mg/L
MLSS change / 24 hours		74	mg/L.day MLSS
Cycle time		306	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		5	
Del MLSS / cycle		16	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		13	mg/L.cycle
Ratio N in $C_5H_7NO_2$		0.12	
Del NH_3-N	A	17	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	4	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	5	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	8	mg/L.cycle N
Estimated assimilated N		2	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		6	mg/L N ((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.02	mg/L.min N

*– total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 24% of the systems nitrogen.

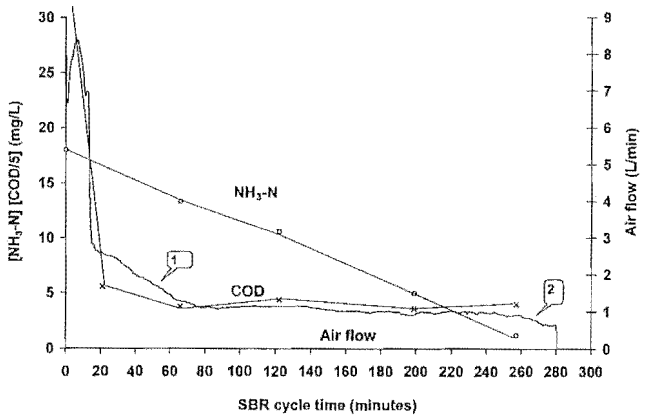


Figure A3.7-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the points of COD and ammonia depletion, points 1 and 2.

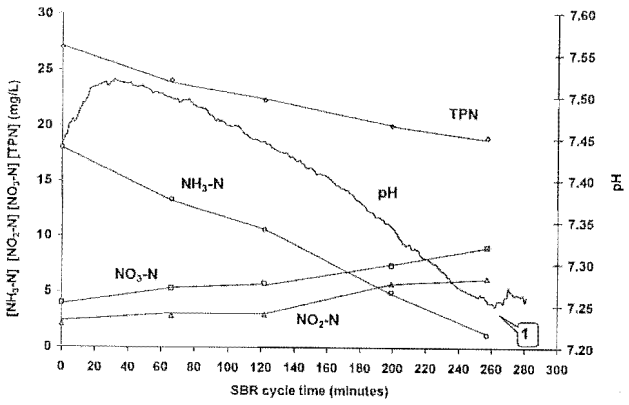


Figure A3.7-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

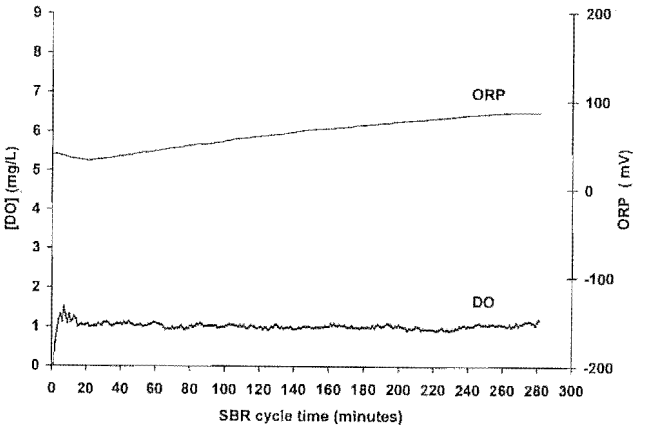


Figure A3.7-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A4.1 - TRACK STUDY ONE (TS1) DOSP 0.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 1 follow

Table A4.2-1 Track study data and nitrogen mass balance calculations TS2

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
	159	21	5	3	31	29			
93	25	15	7	3	28	25	0.07	0.04	0.04
186	33	11	8	4	24	22	0.04	0.04	0.03
262	29	6	9	4	22	19	0.05	0.02	0.03
364	25	0	11	5	19	16	0.06	0.03	0.03
	Loss	Loss	Gain	Gain	Loss	Loss			
	134	21	6	2	13	12			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.05	mg/L.min
		2E-05	mg/L.min.mg MLSS
[MLSS]		3160	mg/L
MLSS change / 24 hours		53	mg/L.day MLSS
Cycle time		434	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		3	
Del MLSS / cycle		16	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		13	mg/L.cycle
Ratio N in $C_5H_7NO_2$		0.12	
Del NH_3-N	A	21	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	6	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	2	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	12	mg/L.cycle N
Estimated assimilated N		2	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		11	mg/L N ((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.03	mg/L.min N

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 36% of the systems nitrogen.

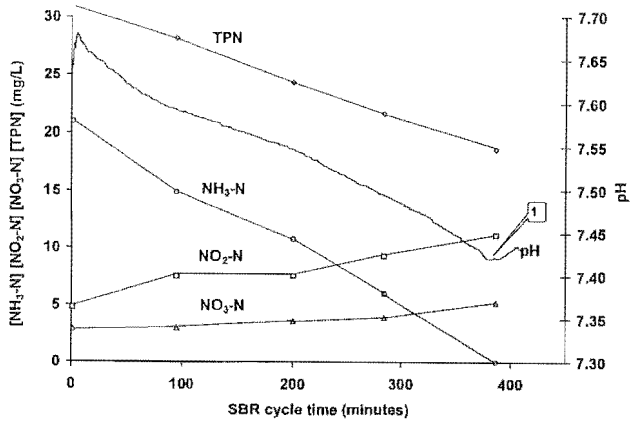


Figure A4.2-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

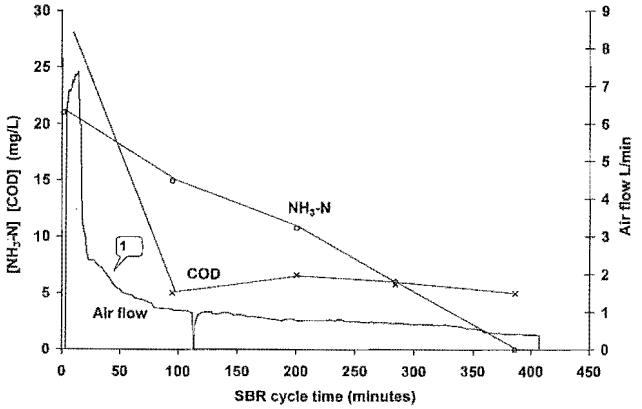


Figure A4.2-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

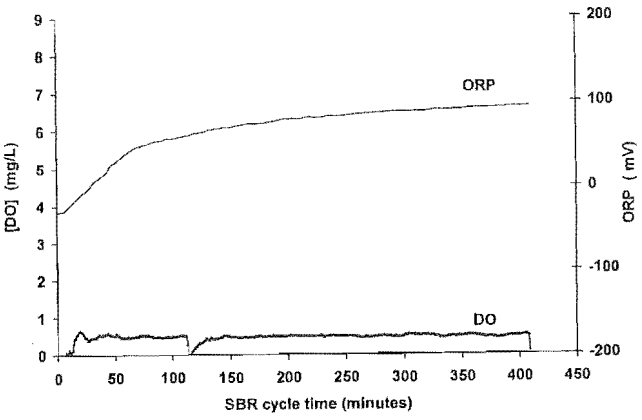


Figure A4.2-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A4.2 - TRACK STUDY TWO (TS2) DOSP 0.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 2 follow

Table A4.2-1 Track study data and nitrogen mass balance calculations TS2

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* – [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss – [Sol TN]
0	171	21.9	3.9	1.2	30	27			
59	45	18.6	4.6	1.6	28	25	0.05	0.03	0.03
193	31	10.8	6.8	1.7	23	19	0.06	0.04	0.04
311	19	5.2	9.0	2.9	20	17	0.05	0.03	0.02
394	23	0.0	9.9	3.1	16	13	0.06	0.05	0.05
	Loss	Loss	Gain	Gain	Loss	Loss			
	148	22	6	2	14	14			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.06	mg/L.min
		2E-05	mg/L.min.mg MLSS
[MLSS]		2929	mg/L
MLSS change / 24 hours		100	mg/L.day MLSS
Cycle time		441	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		3	
Del MLSS / cycle		31	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		25	mg/L.cycle
Ratio N in $C_5H_7NO_2$		0.12	
Del NH_3-N	A	22	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_3-N	B	6	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	2	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	14	mg/L.cycle N
Estimated assimilated N		3	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		11	mg/L N ((+) = loss of N (-) = Gain of N)
Rate Unaccounted N loss		0.03	mg/L.min N

* – total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 37% of the systems nitrogen.

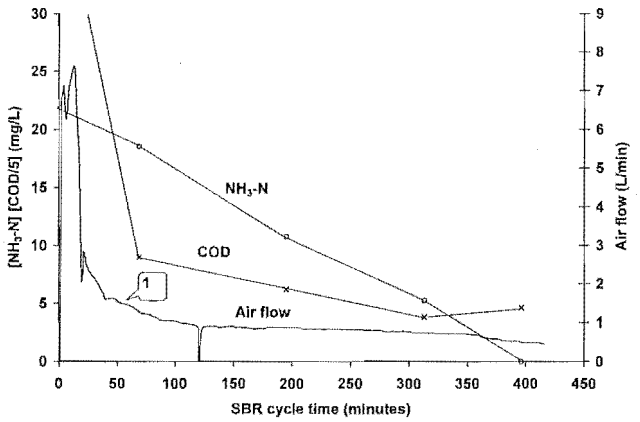


Figure A4.2-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

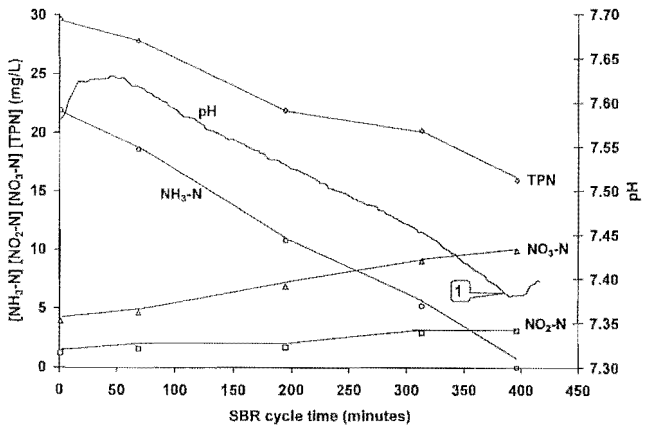


Figure A4.2-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

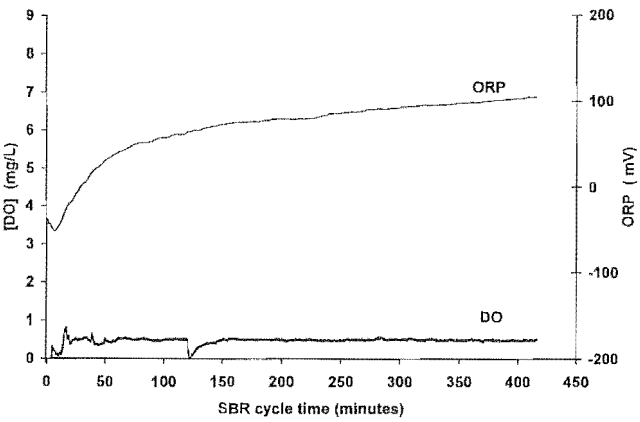


Figure A4.2-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A4.3 - TRACK STUDY THREE (TS3) DOSP 0.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 3 follow

Table A4.3-1 Track study data and nitrogen mass balance calculations

TS3

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_3-N] (B)	[NO_2-N] (C)	[TPN] (D)	* - [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss - [Sol TN]
0	136	21	4	2	30	27			
89	24	15	6	3	26	23	0.06	0.04	0.05
201	35	11	6	3	23	20	0.04	0.03	0.03
303	35	4	8	3	17	14	0.07	0.06	0.05
357	28	1	6	3	15	13	0.05	0.03	0.03
	Loss	Loss	Gain	Gain	Loss	Loss			
	110	20	4	1	15	15			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.05	mg/L.min	
		2E-05	mg/L.min.mg MLSS	
[MLSS]		3380	mg/L	
MLSS change / 24 hours		108	mg/L.day MLSS	
Cycle time		421	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		3		
Del MLSS / cycle		32	mg/L cycle	
VSS/TSS		0.80		
Del MLSS Volatile		25	mg/L cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	20	mg/L cycle N	((+) = loss of N (-) = Gain of N)
Del NO_3-N	B	4	mg/L cycle N	((+) = Gain of N (-) = loss of N)
Del NO_2-N	C	1	mg/L cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	15	mg/L cycle N	
Estimated assimilated N		3	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		12	mg/L N	((+) = loss of N (-) = Gain of N)
Rate Unaccounted N loss		0.03	mg/L.min N	

* - total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 46% of the systems nitrogen.

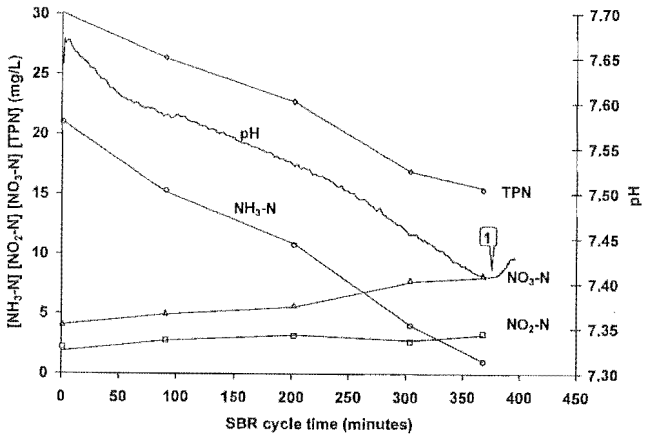


Figure A4.3-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

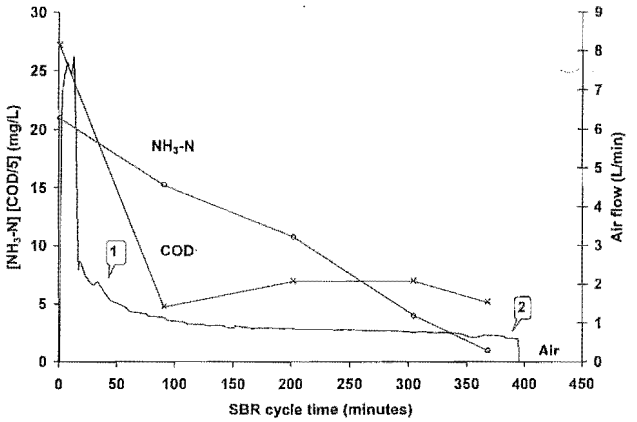


Figure A4.3-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1. There was also a slight indication of the point of ammonia depletion, point 2.

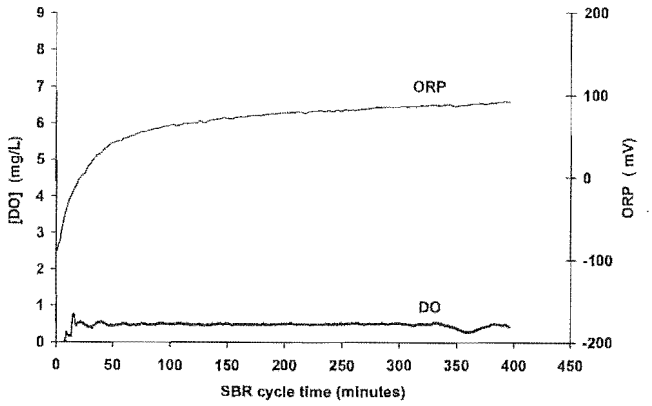


Figure A4.3-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A4.4 - TRACK STUDY FOUR (TS4) DOSP 0.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 4 follow

Table A4.4-1 Track study data and nitrogen mass balance calculations TS4

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	152	20	6	1	29	26			
90	39	15	7	2	27	24	0.05	0.02	0.03
206	28	10	8	2	23	20	0.04	0.04	0.04
329	25	5	10	2	20	17	0.04	0.03	0.02
415	28	0	11	2	15	13	0.06	0.05	0.05
	Loss	Loss	Gain	Gain	Loss	Loss			
	124	20	5	1	14	14			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.05	mg/L.min
		2E-05	mg/L.min.mg MLSS
[MLSS]		2953	mg/L
MLSS change / 24 hours		122	mg/L.day MLSS
Cycle time		470	minutes (Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		3	
Del MLSS / cycle		40	mg/L.cycle
VSS/TSS		0.80	
Del MLSS Volatile		32	mg/L.cycle
Ratio N to $C_5H_7NO_2$		0.12	
Del NH_3-N	A	20	mg/L.cycle N ((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	5	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	1	mg/L.cycle N ((+) = Gain of N (-) = loss of N)
N loss	A+(B+C)	14	mg/L.cycle N
Estimated assimilated N		4	mg/L N to $C_5H_7NO_2$
Unaccounted N loss		10	mg/L N ((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.02	mg/L.min N

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 39% of the systems nitrogen.

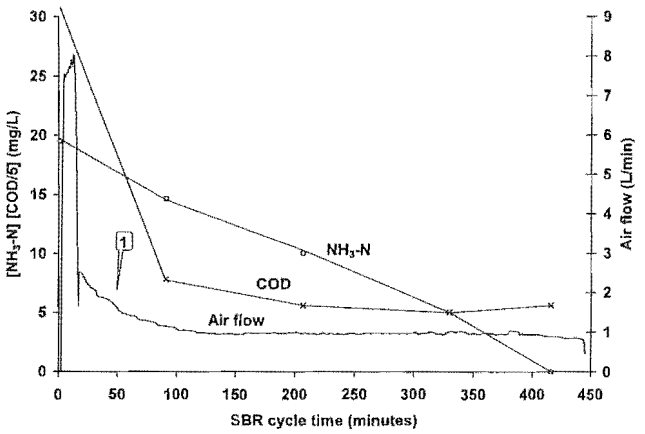


Figure A4.4-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

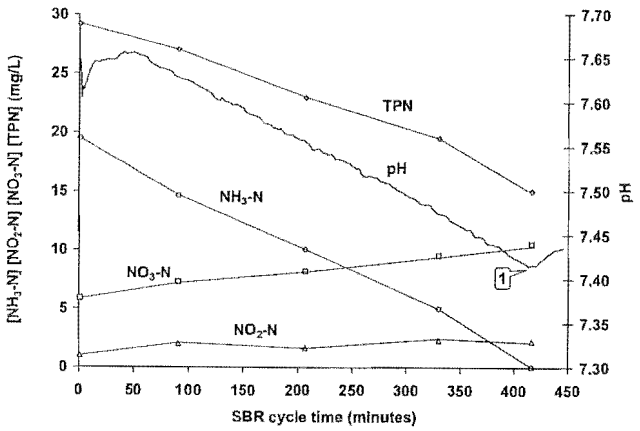


Figure A4.4-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

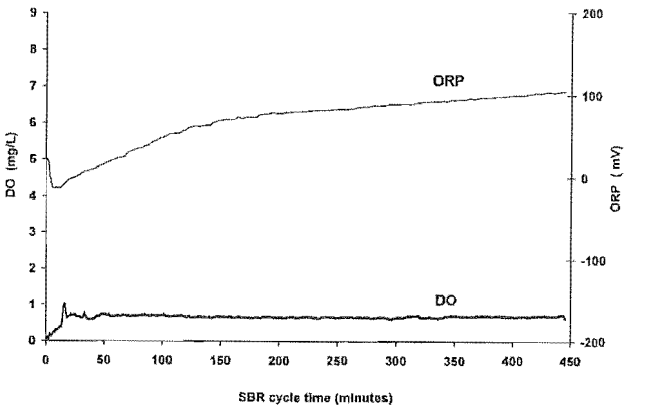


Figure A4.4-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A4.5 - TRACK STUDY FIVE (TS5) DOSP 0.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 5 follow

Table A4.5-1 Track study data and nitrogen mass balance calculations TS5

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	161	20	5	2	30	27			
79	20	15	6	3	27	24	0.06	0.04	0.04
192	28	10	8	2	23	20	0.05	0.04	0.03
270	26	5	9	3	20	17	0.06	0.04	0.04
374	23	0	11	3	17	14	0.05	0.03	0.04
	Loss	Loss	Gain	Gain	Loss	Loss			
	138	20	6	1	13	13			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.05	mg/L.min	
		2E-05	mg/L.min.mg MLSS	
[MLSS]		3343	mg/L	
MLSS change / 24 hours		83	mg/L.day MLSS	
Cycle time		424	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		3		
Del MLSS / cycle		24	mg/L.cycle	
VSS/TSS		0.80		
Del MLSS Volatile		20	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	19.8	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	5.6	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	0.9	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	13.3	mg/L.cycle N	
Estimated assimilated N		2.4	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		10.9	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.03	mg/L.min N	

* ~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 41% of the systems nitrogen.

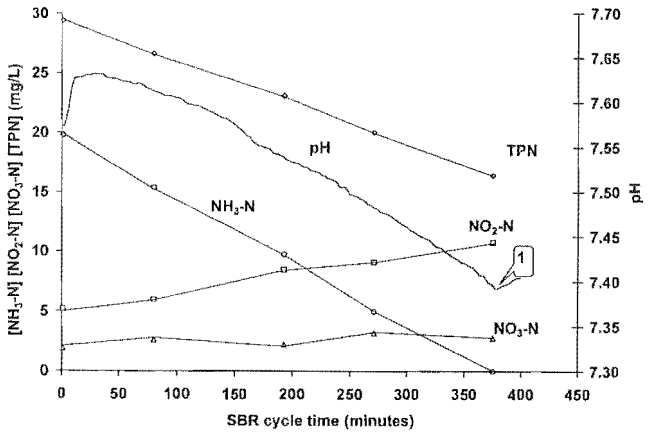


Figure A4.5-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

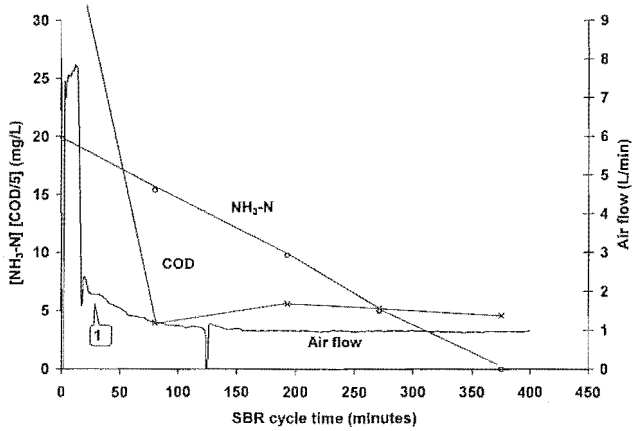


Figure A4.5-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

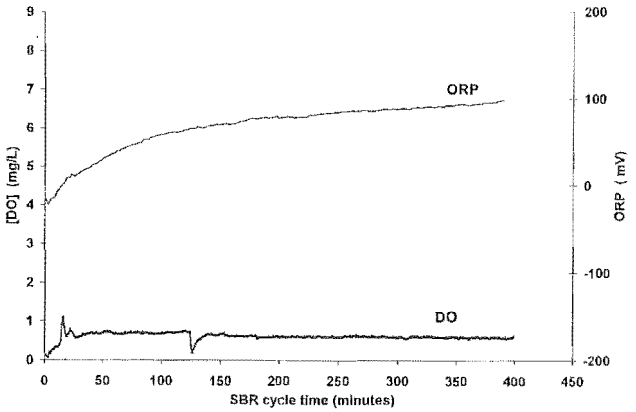


Figure A4.5-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A4.6 - TRACK STUDY SIX (TS6) DOSP 0.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 6 follow

Table A4.6-1 Track study data and nitrogen mass balance calculations TS6

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	106	18	6	2	29	26			
83	29	15	6	1	24	22	0.05	0.07	0.06
166	31	9	7	2	21	19	0.04	0.02	0.02
333	30	3	9	2	18	15	0.04	0.03	0.03
400	20	1	10	2	16	14	0.03	0.02	0.02
	Loss	Loss	Gain	Gain	Loss	Loss			
	86	17	5	0	13	12			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.04	mg/L.min	
		1E-05	mg/L.min.mg MLSS	
[MLSS]		3344	mg/L	
MLSS change / 24 hours		153	mg/L day MLSS	
Cycle time		452	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		3		
Del MLSS / cycle		48	mg/L cycle	
VSS/TSS		0.80		
Del MLSS Volatile		38	mg/L cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	17	mg/L cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	5	mg/L cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	0	mg/L cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	12	mg/L cycle N	
Estimated assimilated N		5	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		7	mg/L N	((+) = loss of N (-) = Gain of N)
Rate unaccounted N loss		0.02	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 32% of the systems nitrogen.

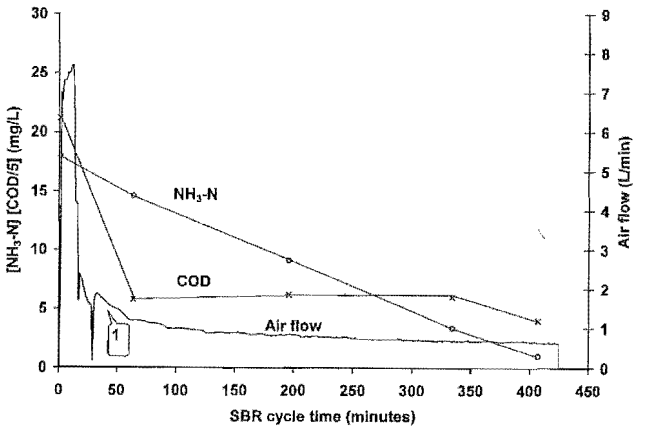


Figure A4.6-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

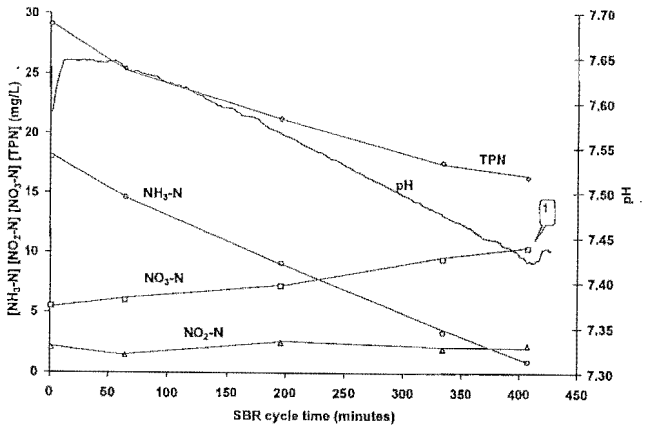


Figure A4.6-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

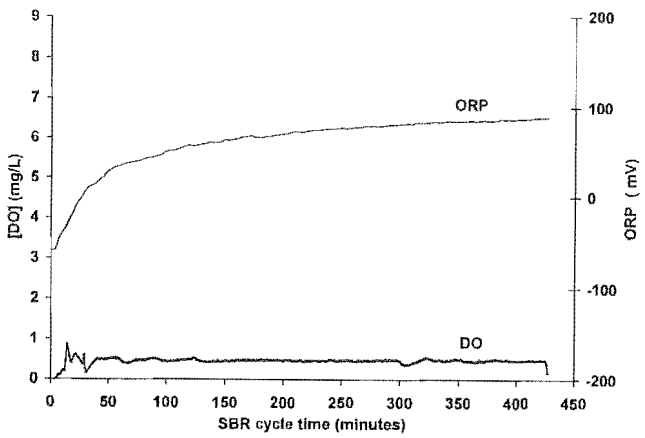


Figure A4.6-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX A4.7 - TRACK STUDY SEVEN (TS7) DOSP 0.5

The biochemical data, nitrogen mass balance calculations, and online data for track study 7 follow

Table A4.7-1 Track study data and nitrogen mass balance calculations TS7

TRACK STUDY

Aeration time	[COD]	[NH_3-N] (A)	[NO_2-N] (B)	[NO_3-N] (C)	[TPN] (D)	* ~ [Sol TN] (A+B+C)	Rate-loss [NH_3-N]	Rate-loss [TPN]	* Rate-loss ~ [Sol TN]
0	170	23	5	2	32	29			
70	24	17	5	1	27	24	0.08	0.07	0.08
195	19	12	7	2	23	20	0.04	0.03	0.03
295	32	7	9	1	20	17	0.05	0.03	0.03
406	23	0	10	2	15	13	0.08	0.06	0.04
	Loss	Loss	Gain	Gain	Loss	Loss			
	147	23	5	1	17	17			
Minutes	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L.min	mg/L.min	mg/L.min

NITROGEN MASS BALANCE

Average rate nitrification		0.06	mg/L.min	
		2E-05	mg/L.min.mg MLSS	
[MLSS]		3256	mg/L	
MLSS change / 24 hours		105	mg/L.day MLSS	
Cycle time		471	minutes	(Aerobic + Settle + 10 minutes fill and decant)
Cycles / day		3		
Del MLSS / cycle		35	mg/L.cycle	
VSS/TSS		0.60		
Del MLSS Volatile		28	mg/L.cycle	
Ratio N in $C_5H_7NO_2$		0.12		
Del NH_3-N	A	23	mg/L.cycle N	((+) = loss of N (-) = Gain of N)
Del NO_2-N	B	5	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
Del NO_3-N	C	1	mg/L.cycle N	((+) = Gain of N (-) = loss of N)
N loss	A-(B+C)	17	mg/L.cycle N	
Estimated assimilated N		3	mg/L N to $C_5H_7NO_2$	
Unaccounted N loss		13	mg/L N	((+) = loss of N (-) = Gain of N)
Rate Unaccounted N loss		0.03	mg/L.min N	

*~ total soluble nitrogen (less organic N)

The nitrogen mass balance procedure accounted for all but 46% of the systems nitrogen.

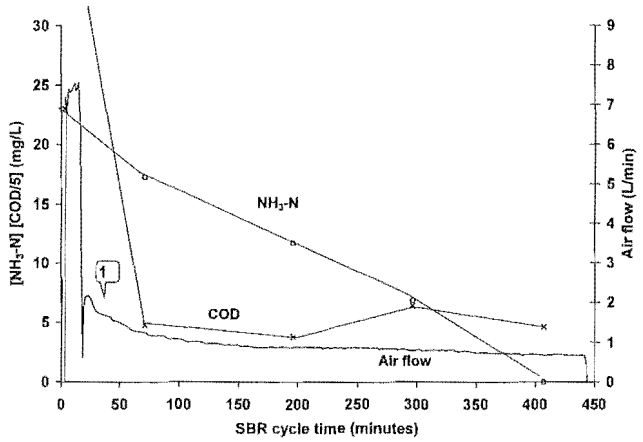


Figure A4.7-2 Air flow rate [ammonia nitrogen], and [COD]

The air flow rate profile provided an indication of the point of COD depletion, point 1.

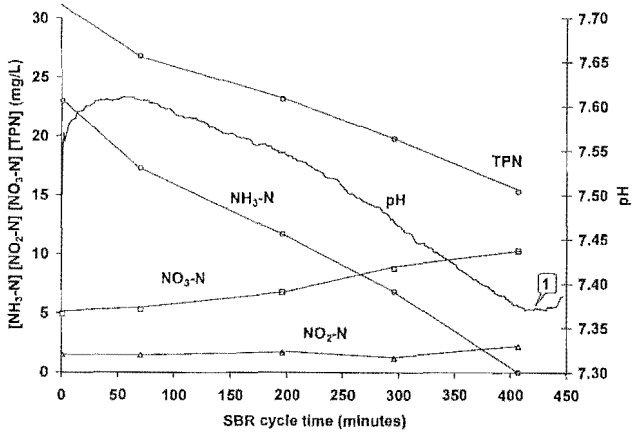


Figure A4.7-1 pH profile and [soluble nitrogen]

The pH profile had an ammonia valley feature at the point of ammonia depletion, point 1. The detection algorithm successfully identified the valley and terminated the aeration phase.

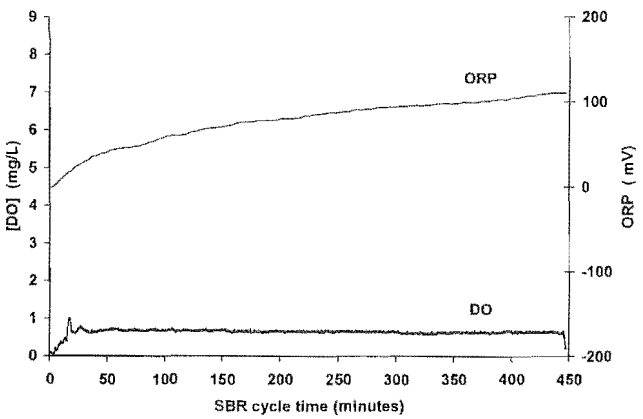
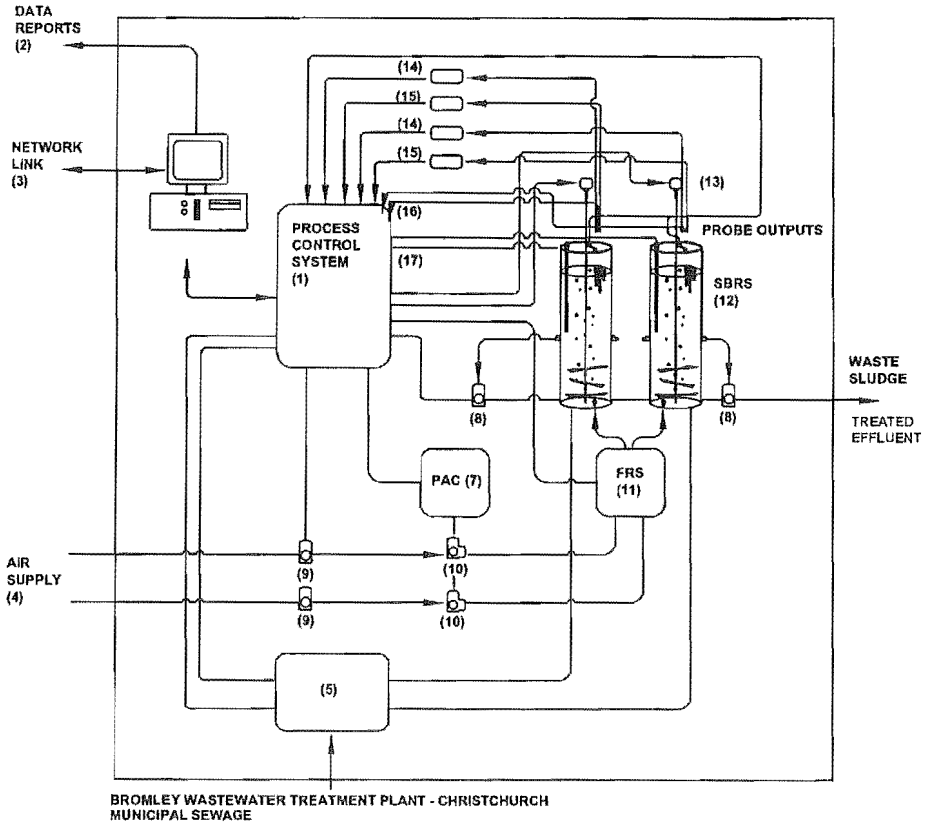


Figure A4.7-3 [DO] and ORP

The ORP profile failed to show any features that could be correlated to the biochemical events.

APPENDIX B1 PHOTOS OF EXPERIMENTAL HARDWARE

To help identify items some photos also have numbers beside specific pieces of hardware, these numbers can be cross referenced to the system diagram below to obtain a description.



KEY

(1) Process controller, microprocessor control, controlled and monitored on Athlon PC. Box incorporates 16 analogue inputs, 16 digital inputs, and 16 digital outputs.
(2) Online real-time data reports for the analysis of treatment process
(3) Network link allowing for remote access to process control system, for example via intranet and internet.
(4) Regulated compressed air supply
(5) 500Lcapacity cold wastewater storage with submersible feed pumps
(6) Immersion heated water bath
(7) (PAC) Proportional air valve controller
(8) Waste solenoids
(9) Air solenoid
(10) Variable rate air solenoids
(11) (FRS) Electronic flow rate sensors
(12) 10L capacity sequencing batch reactors
(13) Mixers
(14) DO meters
(15) pH meters
(16) ORP cables
(17) Fill control pressure transducers

Figure B1-1 System overview

APPENDIX B1 PHOTOS OF EXPERIMENTAL HARDWARE

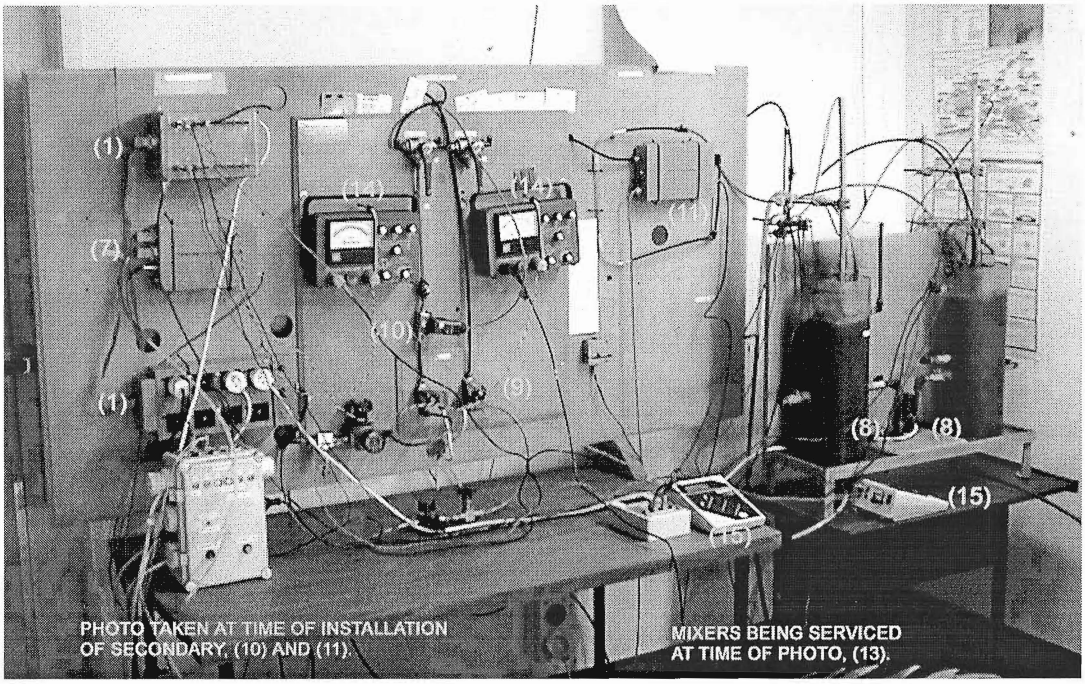


Figure B1-2 Main control board with reactors

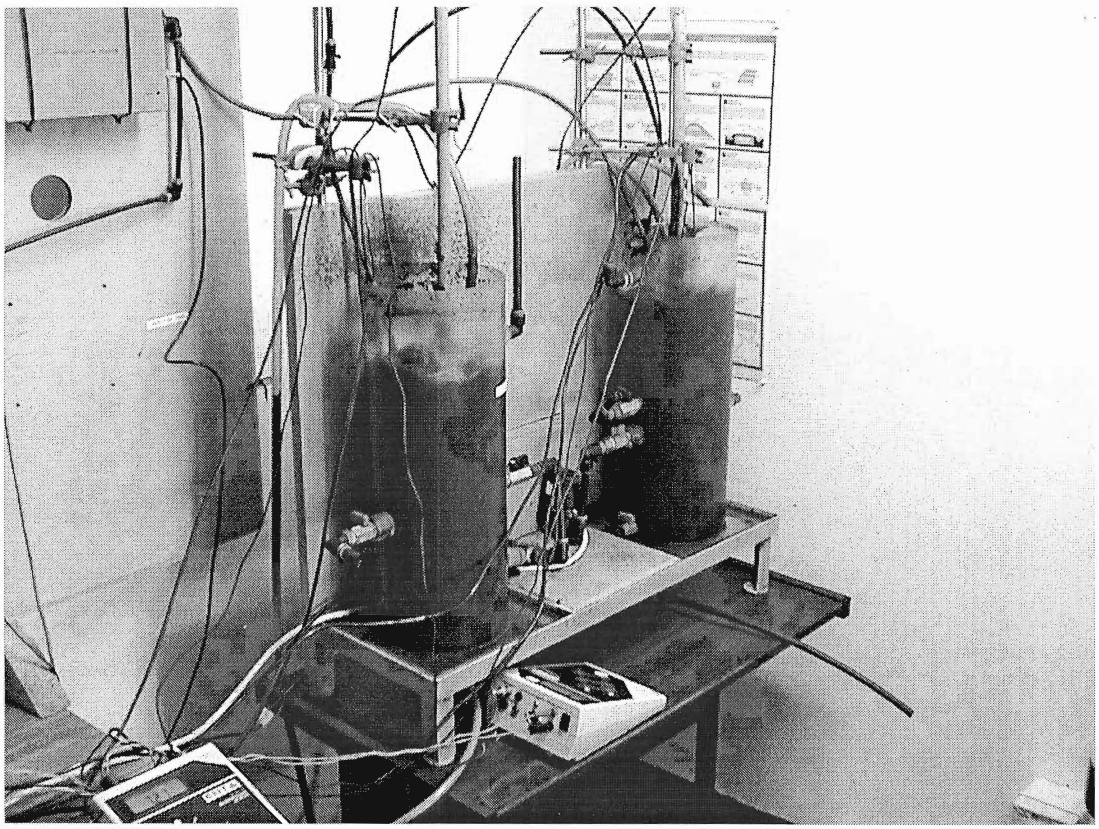


Figure B1-3 Close up of both reactors in operation

APPENDIX B1 PHOTOS OF EXPERIMENTAL HARDWARE

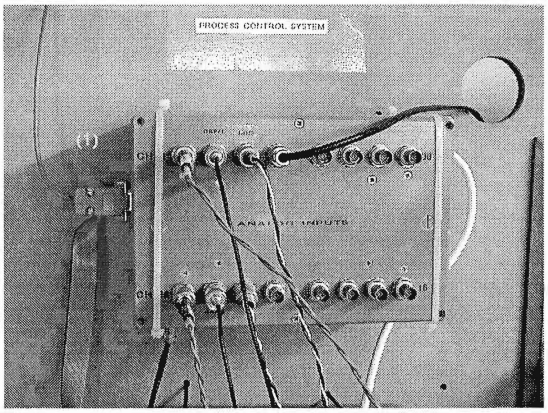


Figure B1-4 Microprocessor based process control system

Figure B1-7 Electronic air flow rate sensor (Box duplicated for second sensor)

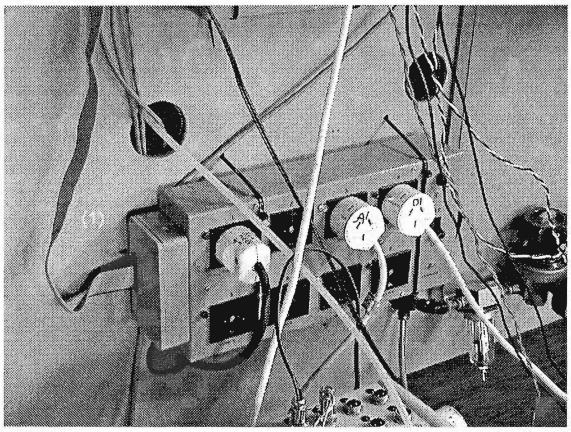


Figure B1-5 Switched 230 volt outputs (Also part of process control system)

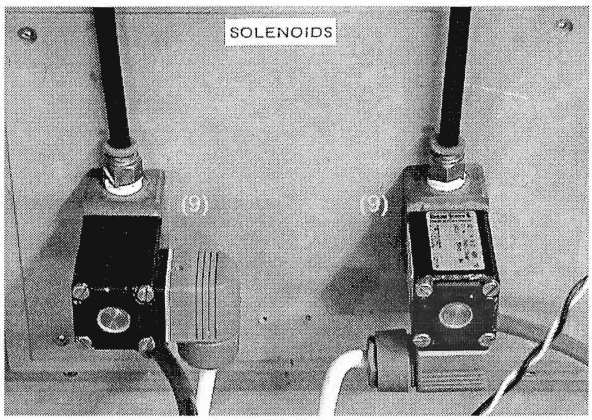


Figure B1-8 On/Off upstream air solenoids

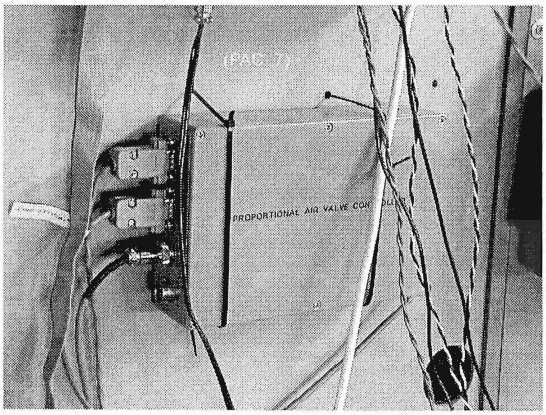


Figure B1-6 Proportional air valve controller

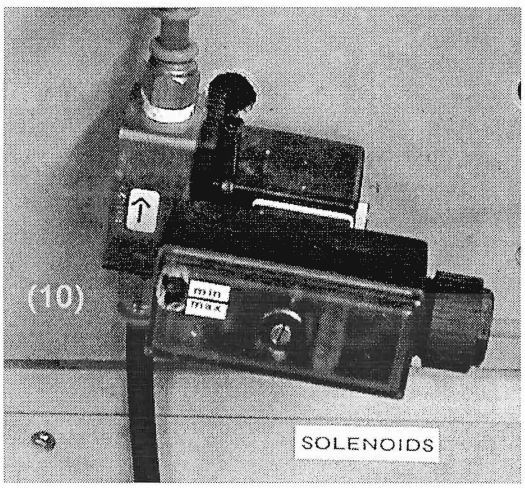


Figure B1-9 Variable rate air solenoid (1 of 2)

APPENDIX B1 PHOTOS OF EXPERIMENTAL HARDWARE

Figure B1-10 Computer linked to process control system

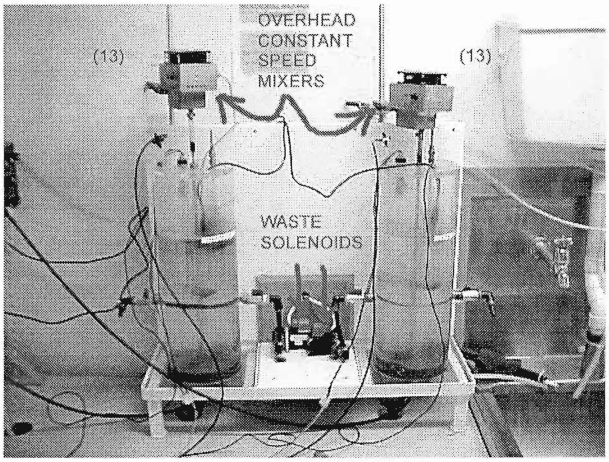


Figure B1-13 Mixing and wasting hardware

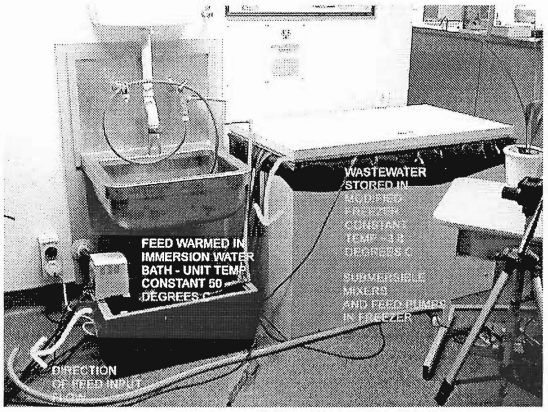


Figure B1-11 Feed storage and supply equipment

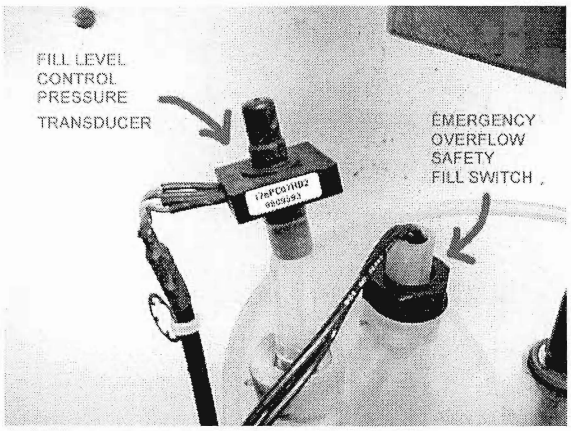


Figure B1-12 Fill control equipment

APPENDIX B2 SEQUENCING BATCH REACTOR OPERATIONAL PARAMETERS

Two reactors were built, each had a usable volume of 8L. This allowed for a wastewater consumption of around 32 L/day or 224 L/week. With the operation of two reactors in parallel this amounted to the consumption of approx 450 L/week of wastewater.

The largest wastewater cooler that could be purchased was 500 L, thus the decision to use an 8 L reactor limited the need for wastewater collection from the main wastewater plant to frequencies of about once per week.

Operational parameters for the sequencing batch reactors used in this research follow,

- Percentage of volume decanted each cycle = 50%.
- Estimated length of Cycle = 3 hours, thus cycles per day = $\left\{\frac{24hours}{day}.\frac{cycle}{3hours}\right\}=\frac{8cycles}{day}$
- Estimated flow per day = 4L per cycle, thus flow per day = $\left\{\frac{8cycles}{day}.\frac{4L}{cycle}\right\}=\frac{32L}{day}$
- The measured influent total [COD] was 650 mg/L. Therefore the initial [COD] = 650 mg/L x 50% reactor retained = 325 mg/L. The initial [BOD_5] ~325 mg/L x 75% ~280 mg/L.
- Operational [MLSS] was around 3000 mg/L. Recommended [MLSS] range for full-scale nitrifying sequencing batch reactors is 1500-5000 mg/L
- Hydraulic residence time (HRT)

$$\left\{8Lvolume-rct.\frac{day}{32L}Flow.\frac{24hours}{day}\right\}=6hours$$

Recommended HRT for full-scale (nitrifying) sequencing batch reactor
Range 12-50 hours

- Volumetric loading

$$\left\{\frac{280mg}{L}.BOD_5.\frac{32L}{day}Flow.\frac{1}{8L}Volume-rct.\frac{g}{1000mg}.\frac{kg}{1000g}.\frac{1000L}{m^3}\right\}=1.12\frac{kg}{m^3.day}\frac{BOD_5-applied}{Rct-volume}$$

Recommended volumetric loading for full-scale (nitrifying) sequencing batch reactor
Range 0.08 – 0.240 $\frac{kg}{m^3.day}\frac{BOD_5-applied}{Rct-volume}$

- Food to microorganism ratio (F/M)

$$\left\{280\frac{mg}{L}.BOD_5.\frac{1}{6hours}HRT.\frac{24hours}{day}.\frac{g}{1000mg}.\frac{kg}{1000g}.\frac{L}{3000mg}[MLSS].\frac{1000mg}{g}.\frac{1000g}{kg}\right\}=0.371\frac{kg}{kg.day}\frac{BOD_5-applied}{MLVSS}$$

Recommended F/M range for full-scale (nitrifying) sequencing batch reactor
Range 0.05 – 0.30 $\frac{kg}{kg.day}\frac{BOD_5-applied}{MLVSS}$

It was not physically possible to operate a lab scale reactor within the ranges suggested for full-scale facilities. The ranges for full-scale facilities are provided as a comparison only and were obtained from Metcalf and Eddy (2001)

APPENDIX B3 DETERMINATION OF AERATION SYSTEM EFFICIENCY

The transfer of air from the gas to the liquid phase was necessary to supply oxygen to the processes. Air was pumped into the reactor through an aquarium type porous stone diffuser.

The gas transfer properties of the system were analyzed to assess aspects such as the rate and efficiency of oxygen transfer. The transfer efficiency of the system was determined using the procedure outlined in Metcalf and Eddy (2001). As the aeration rate was < 3 L/min a series of aeration rates from 0-3 L/min were selected. To enable accurate readings to be taken a Gas Chromatograph (GC) lab grade micro air flow controller was fitted. The actual flow rates were determined manually by the water displacement method as illustrated in Figure B3-1.

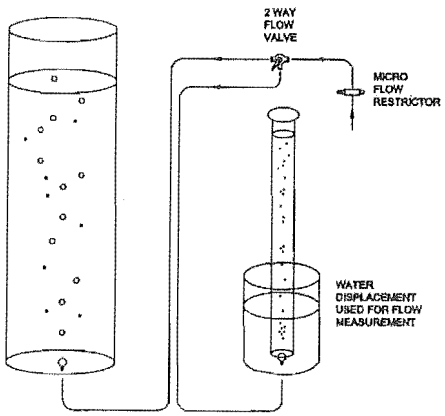


Figure B3-1 Experimental hardware used to determine oxygen transfer parameters.

The procedure involved filling the reactor with clean water. The dissolved oxygen was removed from the water by the addition of sodium sulphite. The water was then re-oxygenated to near saturation level. This procedure was repeated for a series of DO flow rates while readings were manually taken for [DO] versus time. Figure B3-2 illustrates the oxygen transfer rates. The dissolved oxygen transfer rates were determined from the slope of the profiles; the slope from 0-5 minutes was taken to calculate a transfer rate in terms of mg/L.min. By difference of air supplied to air transferred the efficiency was able to be obtained directly. The oxygen mass transfer coefficient was determined using equation B3-1 from Metcalf and Eddy (1991). Table B3-1 shows the experimental data for the 857 mL/min flow rate while Table B3-2 contains a summary of the oxygen transfer parameters for the different flow rates.

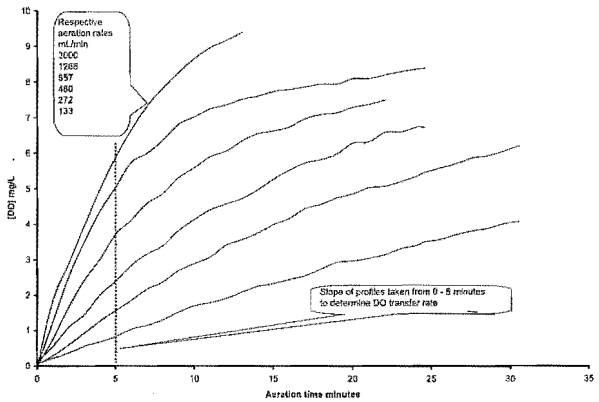


Figure B3-2 Dissolved oxygen concentration during the re-oxygenation process.

$$K_La = 2.303\left(\frac{\log Ct_1 - \log Ct_2}{t_2 - t_1}\right)(60)$$

Equation B3-1 Oxygen mass transfer coefficient in clean water.

Table B3-1 Experimental data for 857 mL/min flow rate.

Time min	[DO] mg/L	C_s-C_t mg/L
2	1.7	7.6
5	3.7	5.6
12	5.6	3.7
16	6.7	2.6
23	7.5	1.8

C_s = 9.3 mg/L @ 20 °C

Example calculation – Determination of K_La for 857 mL/min flow rate.

Using equation B3 -1 $K_La = 2.303\left(\frac{\log 7.6 - \log 1.8}{23-2}\right)(60)$

$K_La = 2.303\left(\frac{0.626}{21}\right)(60) \longrightarrow K_La = 4.1\ h^{-1}$

Table B3-2 Summary of the main dissolved oxygen transfer parameters.

Parameter	Units	Values					
Flow rate	mL/min	134	272	480	857	1266	3000
O_2 supply rate	mg/L.min	4	9	16	29	42	100
Transfer rate	mg/L.min	0.2	0.3	0.4	0.7	0.8	1.0
Transfer efficiency	%	3.5	3.6	2.7	2.4	2.0	1.0
K_La	h^{-1}	1.1	2.3	3.3	4.8	6.2	16

APPENDIX B4 PROCESS CONTROL SOFTWARE AND CONTROL ALGORITHMS

A software package was developed using the Lab View software package from National Instruments.

The software package allowed for ORT monitoring and control via pH, air flow, [DO], and ORP. Control was achieved by the input of appropriate algorithms which provided for the detection of certain profile features that had been correlated to biological events.

pH CONTROL ALGORITHM

ORT control was only implemented into the mix-aeration phase and this was achieved by the use of $\frac{d^2 pH}{dt^2}$.

The sequence behind the $\frac{d^2 pH}{dt^2}$ algorithm is illustrated in Figure B4-1.

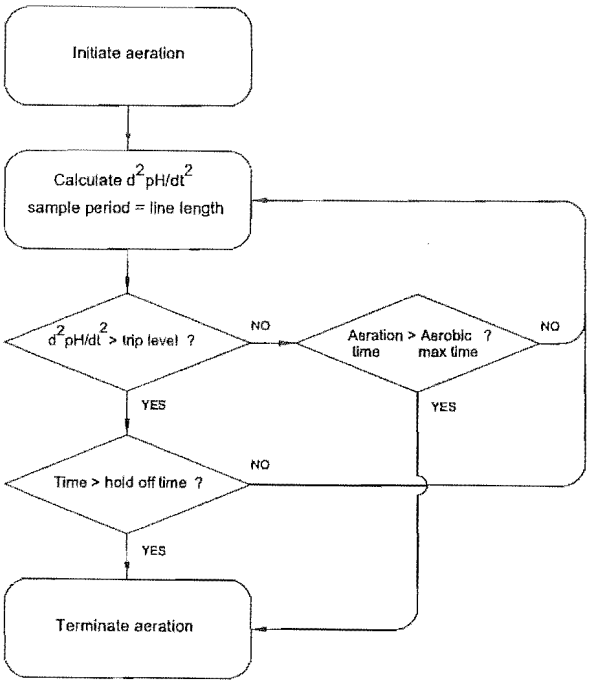


Figure B4-1 Sequence behind the pH control algorithm

The second derivative of pH has also been used by Peng *et al* (2003) who detected the depletion of nitrate nitrogen by using the second derivative of pH to identify the point at which the nitrate apex occurred. The pH control algorithm in this research allowed for the input of three variables. The first variable was the **line length**; this specified the size of the window the second derivative would cover, (usually set to around 30 minutes). The next variable was the second derivative **trip level** or set point. When the calculated value exceeded the set point it indicated the pH profile had probably reached the ammonia valley. The trip level was usually set to about 0.001. The size of the trip level was important as a low value could result in false triggers as a result of spikes or noise on the pH profile while a high value could result in failure to detect the ammonia valley.

The final variable was the **hold off time.** This allowed for a redundant period at the start of the cycle in which the algorithm would not be applied. This was important because the pH initially increased due to CO_2 stripping from the reactor and then decreased again due to nitrification activity; thus, the application of the algorithm from time zero could result in a false trigger.

Included within Figure B5-1 is the **aerobic max time**, a variable set as a default aeration time for use in case the algorithm failed to detect the ammonia valley.

DO CONTROL ALGORITHM

Another sequence within the software allowed control of the dissolved oxygen concentration, illustrated in Figure B4-2. Note that this sequence also included the output from the pH control algorithm.

APPENDIX B4 PROCESS CONTROL SOFTWARE AND CONTROL ALGORITHMS

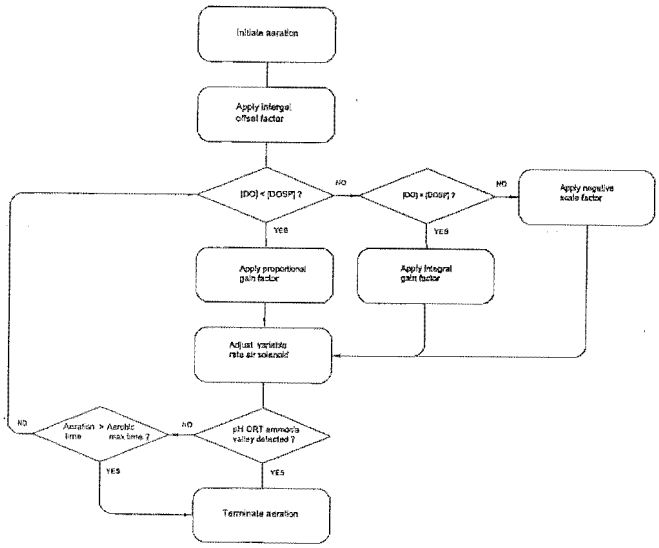


Figure B4-2 Sequence used to control dissolved oxygen concentration

The control of the dissolved oxygen concentration required the input of a number of variables; these have been presented in Table B4-1.

Table B4-1 Variables used to control the dissolved oxygen concentration

Aeration control variables	Purpose
DOSP	Desired [DO]
Maximum aeration time	Terminate aeration if ORT control fails
Proportional gain adjustment factor	Used to adjust air flow when [DO] < DOSP
Integral gain factor	Used to adjust air flow when [DO] = DOSP
Negative scale factor	Used to adjust air flow when [DO] > DOSP
Integral offset factor	Additional initial air flow under specific conditions

To control the dissolved oxygen concentration the system had to manage the air flow rate to the reactor by adjusting a variable rate air solenoid. This was achieved by the use of a "number dump"; the degree to which the valve would open was dependent upon a value generated from this dump. Using this value the control software could adjust the air flow rate from 0-9 L/min over 256 graduations (8 Bit system).

The numbers for the dump were generated from the difference between the actual [DO] and the DOSP. This generated a number called the **DO proportional gain**.

For example if the DOSP was 3.0 mg/L and the actual [DO] was 0.6 mg/L the (difference) DO proportional gain would be calculated as 3.0 – 0.6 = 2.4. Providing a larger number than say DOSP 3.0 mg/L - [DO] 2.5 mg/L = 0.5. A larger DO proportional gain resulted in a larger valve opening-air flow rate.

A **proportional gain adjustment factor** allowed the proportional gain to be adjusted i.e. the DO proportional gain would be calculated (say 3.0 mg/L – 0 mg/L = 3.0) and then multiplied by the factor i.e. 50% * 3.0 = 1.5.

The **integral gain factor** was used to maintain the DO flow rate when the proportional gain reached zero, (i.e. when the DOSP was reached).

When the [DO] was higher than the DOSP the **negative scale factor** was implemented. (it activated when the proportional gain was negative). The negative scale factor was multiplied by the proportional gain before the number was added to the dump, in effect adjusting the rate at which the air flow rate was reduced and the rate at which the [DO] was reduced.

In some situations the proportional gain method could not ramp up the air flow fast enough. For example in situations were a low DOSP was specified the resulting proportional gain was also low. To ensure the DO flow rate increased fast enough in these conditions a variable called the **integral offset factor** was included providing an initial boost to the dump to jump start the process.

APPENDIX B4 PROCESS CONTROL SOFTWARE AND CONTROL ALGORITHMS

SELF ANALYTICAL ROUTINES

The control software also allowed for the development of self analytical routines (i.e. routines that could allow the computer to grade its own performance and make adjustments to the process control parameters) that is, it could detect if a cycle did not reach a set point within a reasonable time and set a new more appropriate set point for future cycles.

GRAPHICAL USER INTERFACE (GUI) TO CONTROL SYSTEM

Control of the system was achieved via a graphical user interface (GUI). The main window displaying the ORT profiles and immediate values is shown in Figure B4-3. The ORT parameters were plotted in real time on screen; the software included various tools for viewing online parameters more closely, (zoom windows and scrolling tools). The immediate values for the ORT parameters were also shown in the column on the right hand side. The ORT pH profile has been highlighted for Figure B4-3, note the operational [DO] at this time was 7.0 mg/L as this photo was taken during the developmental stages of the research.

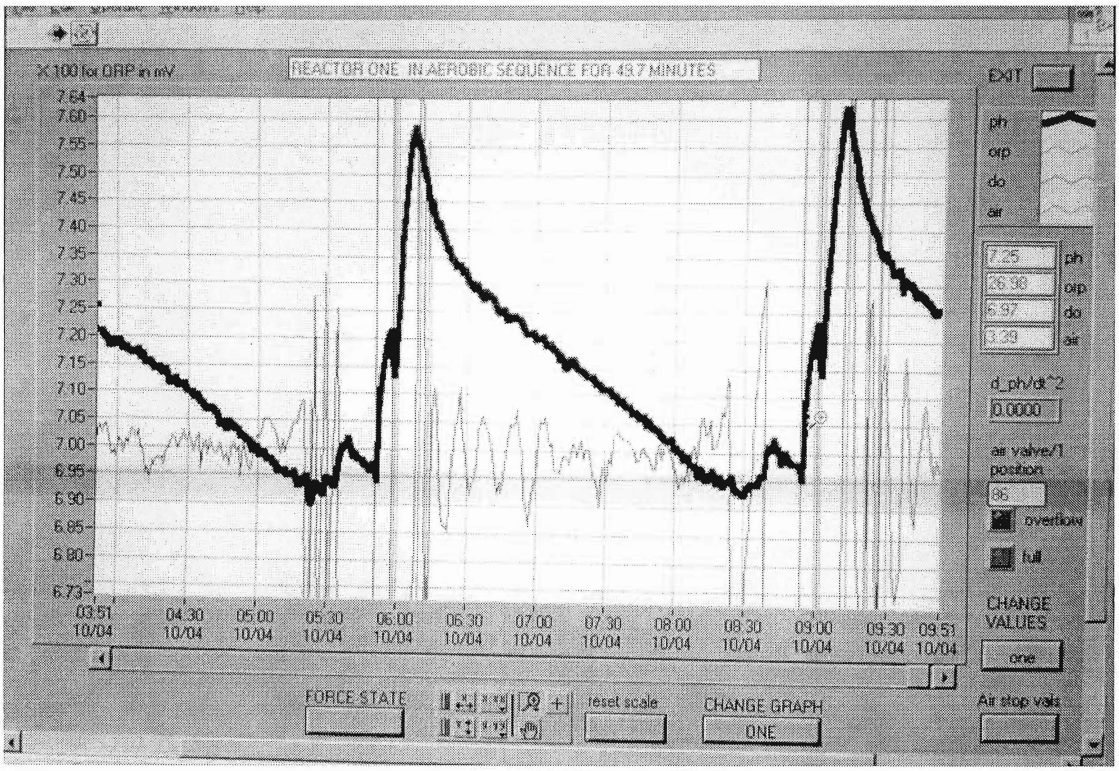


Figure B4-3 Main GUI display with ORT pH profile made bold

From the main control window there were icons to access other parts of the software; for example, the ammonia valley detection algorithm variables are shown in Figure B4-4. This window could be opened from the main screen via the "Air stop vals" icon, (bottom right on main GUI).

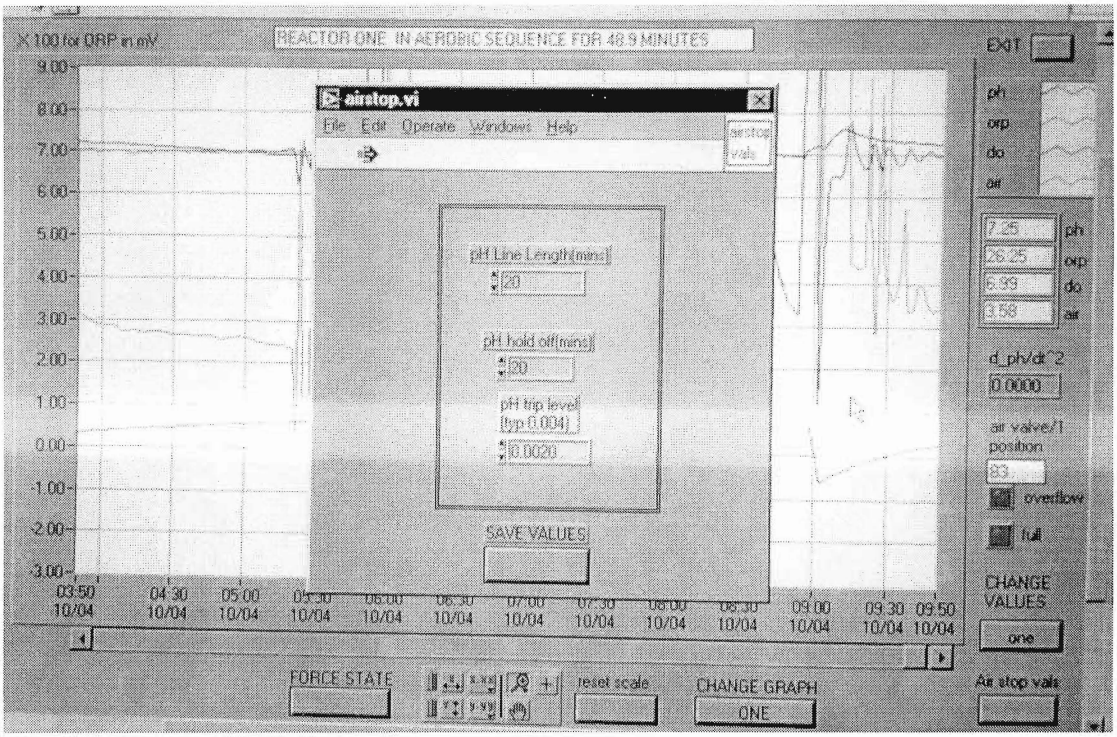


Figure B4-4 Main GUI display with ammonia valley detection window open

The primary control variables and calibration factors were accessed through the "Change values" icon, (lower right main GUI); this opened another window as shown in Figure B4-5. The current sequence along with the control variables could be changed from this window, (located at the bottom are the calibration factors for the ORT parameters).

The force state icon (as shown at the bottom left of Figure B5-4) could be used to access a system over ride window. This is illustrated in Figure B5-6. The over ride window enabled manual control of the main reactor hardware, the manual control decisions superseded those sent by the main control software. This control window was included for maintenance and calibration purposes. With reference to Figure B4-6 the variable rate air valve control goes from 0-255, there were 256 graduations (8 bit) but the scale went to 255 as the software had to use the number 0 as the first graduation.

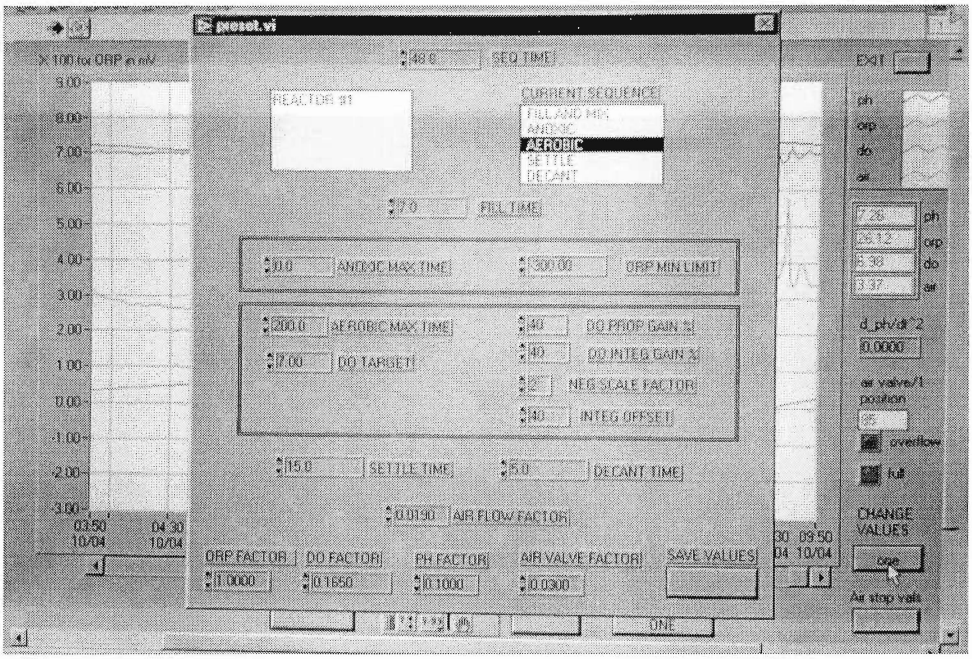


Figure B4-5 Main GUI display with primary control window open

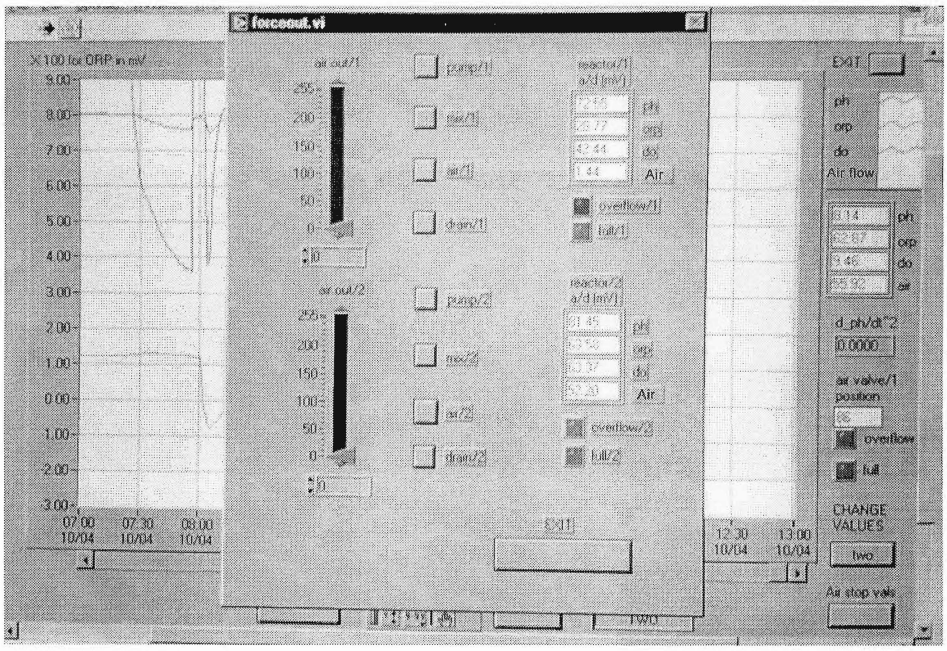


Figure B4-6 Main GUI display with force state control window open

REFERENCES USED IN THIS RESEARCH

Abeling U., Seyfried C.F. (1992) Anaerobic-aerobic treatment of high-strength ammonia wastewater, nitrogen removal via nitrite. *Wat. Sci. Tech.* 26(5-6), 1007-1015.

Abeling U., Seyfried C.F. (1993) Anaerobic-aerobic treatment of potato-starch wastewater. *Wat. Sci. Tech.* 28,165-176.

Abeliovich A., Vonshak A. (1992) Anaerobic metabolism of *Nitrosomonas europea*. *Arch. Microbiology.* 158,267-270.

Addiscott T. (5 February 2000) Making a meal of it. New Scientist- Opinion point-www.newscientist.com 48-49.

Agrawal G.D., Lunkad S.K., Malkhed T. (1999) Diffuse agricultural nitrate pollution of groundwater's in India *Wat. Sci. Tech.* 39(3), 67–75.

Akunna J.C., Bizeau C., Moletta R. (1993) Nitrate and nitrite reductions with anaerobic sludge using various carbon sources: glucose, glycerol, acetic acid, lactic acid and methanol. *Wat. Res.* 27, 1303-1312.

Alex J., Jumar U., Schutze M. (2003) On-line measurement data of wastewater systems via WAP mobile phones. *Wat. Sci. Tech.* 47(2), 205-211.

Al-Ghusain I.A., Huang J., Hao O.J., Lim B.S. (24-30 July 1994) Using pH as a real-time control parameter for wastewater treatment and sludge digestion processes. In 17th Biennial Conference of the International Association on Water Quality, Budapest (Hungary). *Water Quality International.* pp. 159-168.

Al-Ghusain I.A., Hao O.J. (1995) The use of pH as control parameter for aerobic/anaerobic sludge digestion. *Environmental Engineering.* 121 (3), 22—235.

Alleman J.E., Irvine R.L. (1980) Storage-induced denitrification using sequencing batch reactor operation. *Wat. Res.* 14, 1483-1490.

Alleman J.E. (1984) Elevated nitrite occurrence in biological wastewater treatment systems. *Wat. Sci. Tech.* 17, 409-419.

Alleman J.E., Sweeny M.W., Kamber D.M. (1989) Automation of batch waste water treatment systems using programmable logic controllers. *Wat. Sci. Tech.* 10(11),1271-1282.

Anderson I.C., Levine J.S. (1980) Relative rates of nitric oxide and nitrous oxide production by nitrifiers, denitrifiers, and nitrate respirers. *Applied Environmental Microbiology.* 51, 938-945.

Anderson I.C., Homstead J., Burdige D. (1993) A comparison of NO and N_20 production by the autotrophic nitrifier *Nitrosomonas europaea* and the heterotrophic nitrifier *Alcaligenes faecalis*. *Applied Environmental Microbiology.* 59, 3525-3533.

Andreottola G., Foladori P., Ragazzi M. (2001) On-line control of a SBR system for nitrogen removal from industrial wastewater *Wat. Sci. Tech.* 43(3), 93-100.

Anthonisen A.C., Loehr R.C., Prakasam T.B.S., Srinath E.C. (1976) Inhibition of nitrification by ammonia and nitric acid. *J. Wat. Poll. Con. Fed.* 48, 835-853.

Amant P.P., McCarty P.L. (1969) Treatment of high nitrate waste. *Journal of the American Wastewater Association.* 61, 659-663.

Andreadakis A.D. (1993) Physical and chemical properties of activated sludge flocs. *Wat. Res.* 27, 1797-1714.

A.P.H.A. (1998), Standard Methods for the Examination of Water and Wastewater. 17th ed. American Public Health Association, Washington, D.C.

Asano and Levine. (1996) Wastewater reclamation, recycling and reuse: past, present, and future. *Wat. Sci. Tech.* 33(10-11), 1-15.

Asher B., Chozick R., Irvine R.L. (1992) Treatment of a high-strength, mixed phenolic waste in an SBR. *Wat. Env. Res.* 64, 128-133.

Azov Y., Tregubova T. (1995) Nitrification processes in stabilisation reservoirs *Wat. Sci. Tech.* 31(12), 313-319.

Baeza J.A., Gabriel D., Lafuente J. (2002) In-line fast OUR (oxygen uptake rate) measurements for monitoring and control of WWTP. *Wat. Sci. Tech.* 45(4-5), 19-28.

Baker S.C., Ferguson S.J., Lundwig B., Page D.M., Richter O.H., Van R.J. (1998) Molecular Genetics of the Genus *Paracoccus*: Metabolically Versatile Bacteria with Bioenergetic Flexibility. *Microbiology and Molecular Biology Reviews.* 62(4) 1046-1078.

Bang D.Y., Watanabe Y., Noike T. (1995) An experimental study on aerobic denitrification with polyvinyl alcohol as a carbon source in biofilms. *Wat. Sci. Tech.* 32(8), 235-242.

Ballmelle B., Nguyen K.M., Capdeville B., Cornier J.C., Deguin A. (1992) Study of factors controlling nitrite build-up in biological processes for water nitrification. *Wat. Sci. Tech.* 26(5-6), 1017-1025.

Barker P.S., Dold P.L. (1996) Denitrification behaviour in biological excess phosphorus removal activated sludge systems. *Wat. Res.* 27, 617-624.

Bilanovic D., Battistoni F., Cecchi F., Pavan P., Mata-alvarez J. (1999) Denitrification under high nitrate concentration and alternating anoxic conditions, *Wat. Res.* 33(15), 3311-3320.

BIOLAB Scientific (2003) Product technical information.

Bliss P., Barnes D. (1986) Modeling nitrification in plant scale activated sludge. *Wat. Sci. Tech.* 18(6),139-148.

Blume D.J.W., Speece R.E. (1991) A database of chemical toxicity to environmental bacteria and its use in interspecies comparisons and correlations. *Research Journal WPCF.* 63(3), 198-207.

Bock E., Schmidt I., Stuven R., Zart D. (1995) Nitrogen loss caused by denitfying *Nitrosomonas* cells using ammonium or hydrogen as electron donors and nitrite as electron acceptor. *Arch. Microbiology.* 163(1), 16-20.

Bonin P., Gilewicz M. (1991) A direct demonstration of co-respiration of oxygen and nitrogen oxides by *pseudomonas nautical*: some spectral and kinetic properties of the respiratory components. *FEBS Microbiology. Lett.* 80, 183-188.

Brockett O.D. (1972) Further aspects of the microbiological activity of the Mangere oxidation ponds. *Report to the Auckland regional authority research advisory sub-committee. Post Doctoral Studies University of Auckland* Sep 1971-Aug 1973.

Carter J.P., Hsiao Y.H., Spiro S., Richardson D.J. (1995) Soil and sediment bacteria capable of aerobic nitrate respiration. *Applied Environmental Microbiology.* 61(8),2852-2858.

Castignetti D., Hollocher T.C. (1984) Heterotrophic nitrification among denitrifiers. *Applied Environmental Microbiology.* 47, 620-623.

Cecil D. (2003) Controlling nitrogen removal using redox and ammonium sensors. *Wat. Sci. Tech.* 47(11), 109-114.

Chambers B. (1993) Batch operated activated sludge plant for production of high quality effluent at small works. *Wat. Sci. Tech.* 28(10), 251-258.

Charpentier J., Florentz M., David G. (1987) Oxidation Reduction Potential (ORP) Regulation: A way to optimize

pollution removal and energy savings in the low load activated sludge process. *Wat. Sci. Tech.* 19, 645-655.

Charpentier J., Godart H., Martin G., Mongo Y. (1989) Oxidation Reduction Potential (ORP) Regulation as a way to optimize aeration and C,N and P removal: Experimental basis and various full scale examples. *Wat. Sci. Tech.* 21, 1209-1223.

Charpentier J., Menardiere M., Vachon A., Martin G. (1991) ORP as a control parameter in a single sludge biological nitrogen and phosphorus removal activated sludge system. *Water SA*.17(2), 123-132.

Charpentier J., Martin G., Wacheux H., Gilles P. (1998) ORP Regulation of Activated Sludge 15 years of experience. IAWQ 19th Biennial Conference of Vancouver. June 1998.

Chen F., Xia Q., Ju Lu-Kwang. (2003) Aerobic denitrification of *Pseudomonas aeruginosa* Monitored by Online NAD(P) H Fluorescence. *Applied Environmental Microbiology.* 69(11), 6715-6722.

Chen, S. K., Juaw, C.K., Cheng, S.S. (1991) Nitrification and denitrification of high strength ammonium and nitrite wastewater with biofilm reactor. *Wat. Sci. Tech.* 23,1417-1425.

Christensen M.H., Harremoes P. (1977) Biological denitrification of sewage: A literature review. *Prog. Wat. Tech.* 8, 509-555.

Chudoba J. (1989) Activated sludge bulking control. Wastewater treatment technology : Encyclopedia of environmental control technology, Chereminsoff, Gulf Publishing. Vol 3, Chapter 6.

Csikor Z., Czako L., Mihaltz P., Holo J. (1996) Complete nitrogen removal from waste and drinking water in a fluidized-bed bioreactor. *Food. Sci. Tech. Int.* 2(3), 165-171.

Clark H.M., Cooper D., Cutler R. (1996) Dictionary of Chemistry (Text) Third Edition. Oxford University Press. ISBN 0-19-280031-0.

Collivignarelli C., Bertanza G. (1999) Simultaneous nitrification-denitrification process in activated sludge plants: Performance and applicability. *Wat. Sci. Tech.* 40(4-5), 187-194.

Cost (2003) European cooperation in the field of scientific and technical research. http://www.ensic.inpl-nancy.fr/COSTWWTP/

Cohen A., Hegg D., Michele M.de., Song Q., Kasabov N. (2003) An intelligent controller for automated operation of sequencing batch reactors. *Wat. Sci. Tech.* 47(12), 57-63.

Davis L.M., Cornwell A.D. (1998) Introduction to environmental engineering. Third Edition. McGraw Hill. ISBN 0-07-015918-1.

Delgenes J.P., Patureau D. (2004a) Laboratory of environmental biotechnology. The laboratory specializes in the research and development of biological processes for treating effluent and solid waste coming from agricultural, industrial or urban activities. Director : J.P. Delegenes Assistant-Director : D. Patureau LBE-INRA Avenue des Etangs 11100 NARBONNE Phone: +33 (0) 468.425.151 Fax: +33 (0) 468.425.160 http://www.montpellier.inra.fr/narbonne/GM_GB03.html

Delgenes J.P., Patureau D. (2004b) Laboratory of environmental biotechnology. LBE-INRA Avenue des Etangs 11100 NARBONNE Phone: +33 (0) 468.425.151 Fax: +33 (0) 468.425.160 http://www.montpellier.inra.fr/narbonne/GM_GB02.html

Demoulin G., Mervyn C., Goronszy K.W., Forsthuber E. (1997) Co-current nitrification / denitrification and biological P-Removal in cyclic activated sludge plants by redox controlled cycle operation. *Wat. Sci. Tech.* 35(1), 215-224.

Demoulin G., Rudiger A., Goronszy M.C., (2001) Cyclic activated sludge technology – recent operating experience with a 90,000 p.e. plant in Germany. *Wat. Sci. Tech.* 43(3), 331-337.

Dijkman H., Strous M. (1999) Process for ammonium removal from wastewater. http://www.anammox.com/application.html. Patent PCT/NL99/00446. Paper covering this process also available in *Environmental Science and Biotechnology*. (2002). 1, 51-63.

Downes M.T. (1988) Aquatic nitrogen transformation at low oxygen concentrations. *Applied Environmental Microbiology*. 54, 172-175.

Drysdale G.D., Kasan H.C., Bux F. (1999) Denitrification by heterotrophic bacteria during activated sludge treatment. *Wat. SA*. 25(3), 357-362.

Focht D.D., Verstraete W. (1977) Biological ecology of nitrification and denitrification, *Adv. Microb. Ecol.* 1, 135-214.

Francis Garrido (2000) Mechanisms of nitrogen oxide production (N_2O and NO) by soils in aerobic conditions. Thesis ADEME/Conseil Régional de Bourgogne December 08, 2000 at Amphi Orbigny, Faculty of Sciences Gabriel, University of Bourgogne, 21000 Dijon.

Frehmann T., Niemann A., Ustohal P., Geiger W.F. (2002) Effects of real time control of sewer systems on treatment plant performance and receiving water quality. *Wat. Sci. Tech.* 45(3), 229-237.

Frette L., Gejlsbjerg B., Westermann P. (1997) Aerobic denitrifiers isolated from an alternating activated sludge system. *FEMS Microb. Ecol.* 24, 363-370.

Fuerhacker M., Bauer H., Ellinger R., Sree U., Schmid H., Zibuschka F., Puxbaum H. (2000) Approach for a novel control strategy for simultaneous nitrification/denitrification in activated sludge reactors. *Wat. Res.* 34(9), 2499-2506.

Gejlsbjerg B., Frette L., Westermann P. (1998) Dynamics of N_2O Production from activated sludge. *Wat. Res.* 32(7), 2113-2121.

Geraats S.G.M., Hooijmans C.M., Van Neil E.W.J., Robertson L.A., Heijnen J.J., Luyben K.CH.A.M., Kuenen J.G. (1990) The use of a metabolically structured model in the study of growth, nitrification, and denitrification by *Thiosphaera pantotropha*. *Biotech. Bioeng.* 36, 921-930.

Gerber A., Mosert E.S., Winter C.T., de Villiers R.H. (1986) The effect of acetate and other short-chain carbon compounds on the kinetics of biological nutrient removal. *Wat. SA*. 12, 7-12.

Glass C., Silverstein J. (1998) Denitrification, Kinetics of high nitrite concentration water : pH effect on inhibition and nitrite accumulation. *Wat. Res.* 32(3), 831-839.

Goronzy M.C., Demoulin G., Newland M. (1997) Aerated denitrification in full-scale activated sludge facilities. *Wat. Sci. Tech.* 35(10), 103-110.

Goronzy M. (1989) Selector design for high COD wastewaters, a case history. *Wat. Pollut. Control. Fed. Proceedings of the industrial waste symposium, San Francisco.*

Groffman P.M., Verchot L.V. (2004) Denitrification: Underestimation in temperate forest ecosystems. Research report by an institute of ecosystem studies scientist report available at www.ecostudies.org/research/reports/grofrep3.html

Gunatilaka A., Dreher J. (2003) Use of real-time data in environmental monitoring: current practices. *Wat. Sci. Tech.* 47(2), 53-61.

Gupta S.K., Raja S.M., Gupta A.B. (1994) Simultaneous nitrification and denitrification in a rotating biological contactor. *Environmental Technology*. 15, 145-153.

Haandel A C., Ekama G.A., Marais G.R. (1981) The activated sludge process-3 single sludge denitrification. *Wat. Res.* 15, 1135-1152.

Halling S.B., Hjuler H. (1992) Simultaneous nitrification and denitrification with an upflow fixed bed reactor applying clinoptilolite as media. *Water Treatment*. 7, 77-88.

Hanaki K., Wantawin C. (1990) Nitrification at low levels of dissolved oxygen with and without organic loading in a suspended growth reactor. *Wat. Res.* 24(3), 297-302.

Hanaki K., Wantawin C., Ohagaki S. (1990) *Wat. Res.* 24, 289-296.

Hao O.J., Huang J. (1996) Alternating aerobic-anoxic process for nitrogen removal: Process evaluation. *Wat. Env. Res.* 68(1), 83-88.

Harrison D.E.F. (1972) Physiological effects of dissolved oxygen tension and redox potential on growing microorganisms. *Journal of Applied Chemistry and Biotechnology.* 22, 417-440.

Heduit A., Thevenot D.R. (1989) Relation Between Redox Potential and Oxygen Levels in Activated-Sludge Reactors. *Wat. Sci. Tech.* 21, 947-956.

Heijnen J.J., Van Loosdrecht M.C.M. (2004) Delft University clean technology institute, Research into aerobic denitrification and heterotrophic nitrification. Study to identify the optimum process conditions required for aerobic denitrification. The 2004 research is based upon previous experiments with the model organism *Thiosphaera pantotropha* which indicated the specific process conditions in which aerobic denitrification is likely to occur. (Experimental work is based on lab scale SBR activated sludge process). http://www.interduct.tudelft.nl

Heinen N., Norgaard P. (1998) Sequence Sequel. *WQI* May-June.

Helmer C., Kunst S. (1998) Simultaneous nitrification / denitrification in an aerobic biofilm system. *Wat. Sci. Tech.* 30(4-5), 183-187.

Helmo K. (1993) Increasing wastewater plant capacity by online measurement of the microorganism activity and oxygen demand. In: Preprints of *Upgrading of Wastewater Treatment Plants.* Berlin. 21-24 Sept. 317-326.

Henze M. (1989) Carbon sources for denitrification of wastewater. Seminar on nutrient removal from municipal wastewater. 4-6 September 1989.Tampere University. Finland.

Henze M. (1991) Capabilities of biological nitrogen removal processes from wastewater. *Wat. Sci. Tech.* 23, 669-679.

Ho K.M. (1994-5) Biological nutrient removal in activated sludge processes with low F/M sludge bulking control. Ph.D. Thesis. The University of Queensland Australia.

Holman J.B., (2000) Investigation of simultaneous nitrification and denitrification within sequencing batch reactors and the use of ORP as a process control and monitoring parameter. ME Thesis. The University of Canterbury New Zealand.

Holman J.B., Wareham D.G. (2003) Oxidation-reduction potential as a monitoring tool in a low dissolved oxygen wastewater treatment process. *Environmental Engineering.* 129(1), 52-58.

Huang J.C. (1995) Prevention and control of filamentous growth in activated sludge systems. *Water SA.* 21(3), 229-236.

Inamori U., Takahashi T., Sudo R. (1986) Effects of anaerobic conditions on activated sludge processes. *J.Jap. Sew. Wks. Ass.* 23, 61-69.

Irvine R.L., Ketchum (Jr) L.H., Arora M.L., Barth E.F. (1985) An organic loading study of full-scale sequencing batch reactors. *Wat. Poll. Con. Fed.* 57, 847-853.

Irvine R.L., Murthy D.V.S., Arora M.L., Copeman J.L., Heidman J.A. (1987) Analysis of full-scale SBR operation at Grundy Centre, Iowa. *Wat. Poll. Con. Fed.* 2(59), 132-138.

Irvine R.L., Wilderer P.A., Flemming H.C. (1997) Controlled unsteady state processes and technologies-an overview. *Wat. Sci. Tech.* 35(1), 1-10.

Jenkins D., Sezgin M., Parker D.S. (1978) A Unified theory of filamentous activated sludge bulking. *Wat. Poll. Con. Fed.* 50, 362-381.

Jenkins D., Palm J.C., Parker D.S. (1980). Relationship between organic loading and dissolved oxygen concentration and sludge settleability in the completely mixed activated sludge process. *Wat. Poll. Con. Fed.*. 52, 2482-2506.

Jenkins C.J., Mavinic D.S. (1989) Anoxic-aerobic digestion of waste activated sludge: Part II-Supernatant characteristics, ORP monitoring results and overall rating system. *Environmental. Tech. Lett.* 10, 371-384.

Kawakami Y., * (1985) * *Ferment. Tech.* 63, 437-442. *other information unavailable.

Kim H., Hao O.J. (2001) pH and Oxidation-reduction potential control strategy for optimization of nitrogen removal in an alternating aerobic-anoxic system. *Wat. Env. Res.* 73 (1), 95-102.

Kim D.J., Chang J.S., Lee D.I., Han D.W., Yoo I.K., Cha G.C. (2003) Nitrification of high strength ammonia wastewater and nitrite accumulation characteristics. *Wat. Sci. Tech.* 47(11), 45-51.

Hayward K. (1998) BNR's Control Key. WQI Sep-Oct 1998 issue. Pages 14-15.

Ketchum (Jr) L.H., Irvine R.L., Breyfogle R.E., Manning (Jr) J.F. (1987) A comparison of biological and chemical phosphorus removals in continuous and sequencing batch reactors. *Wat. Poll. Con. Fed.* 59, 13-18.

Ketchum (Jr) L.H., Irvine R.L., Dennis R.W. (1979) Sequencing batch reactors to meet compliance. *Water-1978, Amer. Inst,. of Chem Engr. Symposium Series.* 75(190), 186-191.

Ketchum (Jr) L. H., Liao P.C., Irvine R.L. (1978) Economics evaluation of sequencing batch reactors. *Proc 33rd Industrial Waste Conf Purdue University, West Lafayette, Ind*, 357-376.

Ketchum L.H. (1997) Design and physical features of sequencing batch reactors. *Wat. Sci. Tech.* 35(1), 11-18.

Khalil M.A.K., Rasmussen R.A. (1988) Nitrous oxide:trends and global mass balance over 300 years. *Annuals of glaciology.* 10, 73-79.

Killham K. (1986) Heterotrophic nitrification. *Nitrification* (IRL Press Oxford). 117-126.

Koch F.A., Oldham W.K. (1985) Oxidation reduction potential a tool for monitoring control and optimization of biological nutrient removal systems. *Wat. Sci. Tech.* 17, 259-279.

Koch F.A., Oldham W.K., Wang H.Z. (1988) ORP as a tool for monitoring and control in bio-nutrient removal systems. *ASCE/CSCE Environmental Engineering. Conference.* July 12-19, Vancouver BC. 162-170.

Knowles R. (1982) Denitrification. *Microb.Rev.* 46, 43-70.

Krishnamachari S., Clarkson W.W. (1992) Effluent nitrite accumulation in the heterotrophic denitrification of high strength industrial wastewaters. *Environmental Engineering.* 370-375.

Krul J.M. (1976) The relationship between dissimilalatory nitrate reduction and oxygen uptake by cells of an *Alcaligenes* strain in flocs and in suspension and by activated sludge flocs. *Wat. Res.* 10(4), 337-341.

Kshirsagar M., Gupta A.B., Gupta S.K. (1995) Aerobic denitrification studies on activated sludge mixed with *Thiosphaera pantotropha. Environmental Technology.* 16, 35-43.

Kugleman I.J., Spector M. (1988) Nutrient removal in staged biological reactors. *Proceedings 3rd WPCF joint technical seminar on sewage treatment technology May 12-14 1988 Tokyo Japan.* 4-27.

Kugleman I.J., Spector M., Harvilla A., Parees D. (1991) Aerobic denitrification in activated sludge. *Environmental engineering special conference* (Edited by Krenkel P.A.). 312-319. Am. Soc. Civil. Engrs.

Kuenen J.G., Robertson L.A. (1987) Ecology of nitrification and denitrification. Cambridge University Press. pp 161-218.

Langner C. L.., and Hendrix P. F. (1982). Evaluation of a persulfate digestion method for particulate nitrogen and phosphorus. *Wat. Res.* 16, 1451-1454.

Lo K.V., Liao P.H., Van Kleeck R.J. (1990) A full scale sequencing batch reactor treatment of diluted swine wastewater. *Can. Agric. Eng.* 33, 193.

Lo C.K., Yu C.W., Tam N.F.Y., Traynor S. (1994) Enhanced nutrient removal by oxidation reduction potential (ORP) controlled aeration in a laboratory scale extended aeration system. *Wat. Res.* 28(10), 2087.

Lloyd D., Boddy L., Davies K.J.P. (1987) Persistence of bacterial denitrification capacity under aerobic conditions: The rule rather than the exception. *FEMS Microb. Ecol.* 45, 185-190.

Lukow T., Diekmann H. (1997) Aerobic denitrification by a newly isolated heterotrophic bacterium strain TL1. *Bio. Tech. Lett.* 19(11), 1157-1159.

Massone A.G., Gernaey K., Bogaert H., Vanderhasselt A., Rozzi A., Verstraete W. (1996) Biosensors for nitrogen control in wastewaters. *Water Quality International 18th Biennial Confenerce and Exhibition 23-28 June 1996 Singapore.* 1, 183-190.

Masuda S., Watanabe Y., Ishiguro M. (1991) Biofilm properties and simultaneous nitrification and denitrification in aerobic rotating biological contactors. *Wat. Sci. Tech.* 23, 1355-1363.

Matsuo Y., Hosobora K. (1988) *Proc 3rd WPCF/JSWA Joint tech sem on sewage treat tech.* Tokyo. 84-121.

Meinardi C.R., Beusen A.H.W., Bollen M.J.S., Klepper O., Willems W.J. (1995) Vulnerability to diffuse pollution and average nitrate contamination of European soils and groundwater *Wat. Sci. Tech. 31(8), 159–165.*

Meirlaen J., Assel V.J., Vanrolleghem P.A. (2002) Real time control of the integrated urban wastewater system using simultaneously simulating surrogate models *Wat. Sci. Tech. 45(3), 109-116.*

Metcalf and Eddy (1991) Wastewater engineering treatment disposal and reuse. Third Edition (Text). *McGraw Hill Publishers.* ISBN 0-07-041690-7.

Metcalf and Eddy (2001) Wastewater engineering treatment and reuse. *McGraw Hill Publishers.* ISBN 0-07-112250-8.

Moriyama K., Sato K., Harada Y., Washiyama K., Okamoto K. (1990) Renovation of an extended aeration plant for simultaneous biological removal of nitrogen and phosphorus using oxic-anaerobic-oxic process. *Wat. Sci. Tech.* 22(7-8), 61-66.

Moriyama K., Takahashi M., Harada Y. (1993) Retrofitting and operation of small extended aeration plants for advanced treatment – some experiences in Japan. In: Preprints of *Small Wastewater Treatment Plants.* Trondheim (Norway). Tapir Publisher.

Morris J.C., Stumm W. (1967) Redox equilibria and measurements of potentials in the aquatic environment. *Adv. Chem. Series.* No. 67, Article 13, 270-285.

Mosey F. (1985) Redox potential in wastewater treatment. *The Chemical Engineer.* May 1985. 21-24.

Munch E.V., Lant P., Keller J. (1996) Simultaneous nitrifiation and denitrification in bench scale sequencing batch reactors. *Wat. Res.* 30(2), 227-284.

Nakanishi H., Fukagawa M., Takeuchi M., Ishikawa M., Ukita M., Murakami S. (1990) Biological nitrogen removal in a complete mixing type aeration with ORP control. *Wat. Sci. Tech.* 22(7-8), 269.

Neef *et al* (1996). This reference used in discussion on page 97. Please contact the author for further details with respect to this reference. j.holman@civil.canterbury.ac.nz (0064-27-241-7043).

Ng W.J., Sim T.S., Ong S.L., Ng K.Y., Ramasamy M., Tam K.N. (1993) Efficiency of sequencing batch reactor (SBR) in the removal of selected microorganisms from domestic sewage. 27(10), 1591-1600.

Nielsen W.M., Jansen C.J. (1996) The role of the sludge in nitrification inhibition tests. *Wat. Sci. Tech.* 33(6), 93-100.

Nielsen M., Revsbech N.P., Larsen L.H., Jensen L.A. (2002) Online determination of nitrite in wastewater treatment by use of a biosensor. *Wat. Sci. Tech.* 45(4-5), 69-76.

Norcross K.L., (1992) Sequencing Batch Reactors - An overview. *Wat. Sci. Tech.* 26(9-11), 2523-2526.

Novak L., Larrea L., Wanner J., Garcia Heras J.L. (1993) Non-filamentous activated sludge bulking in a laboratory scale system. *Wat. Res.* 27(8), 1339-1347.

NZWWA (1997) Nitrogen elimination in sewage treatment plants. *Water and Wastes in New Zealand.* No 97, September.

O'Neil M., Horan N. (1995) Achieving simultaneous nitrification and denitrification of wastewater at reduced cost. *Wat. Sci. Tech.* 32(9-10), 303-312.

Osada T., Haga K., Harada Y., (1991) Removal of nitrogen and phosphorus from swine wastewater by the activated sludge units with intermittent aeration process. *Wat. Res.* 25(11), 1377-1388.

Otlanabo N.L., (1993) Denitrification of ground water for potable purposes. *WRC report No.403/1/93.*

Oxford dictionary of chemistry (1996) Third edition. Oxford University Press ISBN 0-19-280031-0.

Painter H.A., (1977) Microbial transformations of inorganic nitrogen. *Wat. Sci. Tech.* 8(4-5), 3-29.

Paul E., Plisson-Saune S., Mauret M., Cantet J. (1998) Process state evaluation of alternating oxic-anoxic activated sludge using ORP, pH and DO, *Wat. Sci. Tech.* 38(3), 299-306.

Payne W.J. (1981) *Denitrification.* Wiley. New York.

Patureau D., Davison J., Bernet N., Moletta R. (1994) Denitrification under various aeration conditions in *Comamonas* sp., strain Sgly2. *FEMS. Microb. Ecol.* 14(1), 71-78.

Patureau D., Bernet N., Moletta R. (1996a) Study of the denitrifying enzymatic system of *Comamonas* SP., strain SGLY2, under various aeration conditions with a particular view on nitrate and nitrite reductases. *Curr. Microb.* 32(1), 25-32.

Patureau D., Bernet N., Moletta R. (1996b) Effect of oxygen on denitrification in continuous chemostat culture with *Comamonas* sp., strain SGLY2. *Journal of Industrial Microbiology.* 16, 124-128.

Patureau D., Godon J.J., Dabert P., Bouchez T., Bernet N., Delgenes J.P., Moletta R. (1998) *Microvirgula aerodenitrificans* gen. nov., sp. nov., a new gram-negative bacterium exhibiting co-respiration of oxygen and nitrogen oxides up to oxygen-saturated conditions. *International Journal of Systematic Bacteriology.* 48, 775-782.

Patureau D., Bernet N., Delgenes J.P., Moletta R. (2000) Effect of dissolved oxygen and carbon-nitrogen loads on denitrification by an aerobic consortium. *Applied Microbiology and Biotechnology.* 54(4), 534-542.

Patureau D., Helloin E., Rustrian E., Bouchez T., Delegenes J.P., Moletta R. (2001) Combined phosphate and nitrogen removal in a sequencing batch reactor using the aerobic denitrifier *Microvirgula aerodenitrificans. Wat. Res.* 35(1), 189-197.

Peddie C.C., Koch F.A., Jenkins C.J., Mavinic D.S. (1988) ORP as a tool for monitoring and control of SBR systems for aerobic sludge digestion. *In proceedings of the joint ASCE/CSCE Environmental Engineering Conference, July 12-19 Vancouver Canada.* p.171.

Peddie C.C., Mavinic D.S., Jenkins C.J. (1990) Use of ORP for monitoring and control of aerobic sludge digestion. *Environmental Engineering.* 116(3), 461-471.

Pedersen D.P., Jensen K., Lyngsie P., Johansen H. (2003) Nitrogen removal in industrial wastewater by nitration and denitration 3 years of experience. *Wat. Sci. Tech.* 47(11), 181-188.

Peng Y.Z., Gao J.F., Wang S.Y., Sui M.H. (2002) Use of pH and ORP as fuzzy control parameters of denitrification in SBR process *Wat. Sci. Tech.* 46(4-5), 131-137.

Peng Y.Z., Gao J.F., Wang S.Y., Sui M.H. (2003) Use of pH as fuzzy control parameter for nitrification under different alkalinity in SBR process. *Wat. Sci. Tech.* 47(11), 77-84.

Pipes W.O. (1967) Bulking of activated sludge. *Advanced Applied Microbiology.* 9, 185-234.

Plisson-Saune S., Capdeville B., Mauret M., Daguin A., Baptise P. (1996) Real-time control of nitrogen removal using three ORP bending-points signification control strategy and results. *Wat. Sci. Tech.* 33(1), 275-280.

Pochana K., Keller J., Lant P. (1997) Effect of level and range of dissolved oxygen (DO) on simultaneous nitrification / denitrification (SND). *Proceeding of BNR3 conference.* Brisbane. Australia.

Pochana K., Keller J. (1999) Study of factors affecting simultaneous nitrification and denitrification (SND). *Wat. Sci. Tech.* 39(6), 61-68.

Pochana K., Keller J., Lant P. (1999) Model development for simultaneous nitrification and denitrification. *Wat. Sci. Tech.* 39(1), 235-243.

Poth M. (1986) Dinitrogen production from nitrite by a *Nitrosomonas* isolate. *Applied Environmental Microbiology.* 52(4), 957-959.

Ra C.S., Lo K.V., Shin J.S., OH J.S., Hong B.J. (2000) Biological nutrient removal with an internal organic carbon source in piggery wastewater treatment. *Wat. Sci. Tech.* 34(3), 965-973.

Randal C.W., Buth D. (1984) Nitrite build-up in activated sludge resulting from temperature effects. *Wat. Poll. Con. Fed.* 56, 1039-1044.

Randal C.W., Barnard J.L., Stensel H.D. (1992) Design and retrofit of wastewater treatment plants for biological nutrient removal. *Water quality management library. Volume 5. Technomic Pub. Co. Lancaster PA USA.* 25-56.

Rhee K.S., Lee J.J., Lee S.T. (1997) Nitrite accumulation in a sequencing batch reactor during the aerobic phase of biological nitrogen removal. *Biotechnology letters.* 19(2), 195-198.

Risholt L.O., Schilling W., Erbe V., Alex J. (2002) Pollution based real time control of wastewater systems. *Wat. Sci. Tech.* 45(3), 219-228.

Rittmann B.E., Langeland W.E. (1985) Simultaneous denitrification with nitrification in single-channel oxidation ditches. *Wat. Poll. Con. Fed.* 57(4), 300-308.

Robertson L.A., Kuenen J.G. (1983) *Thiosphaera pantotropha* gen. nov., a facultatively anaerobic, faculatatively autotrophic sulphur bacterium. *Gen. Microb.* 129, 2847-2855.

Robertson L.A., Kuenen J.G. (1984) Aerobic denitrification a controversy. *Arch. Microb.* 139, 351-354.

Robertson L.A. (1988) Aerobic denitrification and heterotrophic nitrification in *Thiosphaera pantotropha* and other bacteria. Ph.D. thesis. Delft University of Technology. The Netherlands.

Robertson L.A., Van Neil E.W.J., Torremans R.A.M., Kuenen J.G. (1988) Simultaneous nitrification and denitrification in aerobic chemostat cultures of Thiosphaera pantoropha. *Applied Environmental Microbiology.* 54(11), 2812-2818.

Robertson L.A., Cornelisse R.De.Vos P., Hadioetomo R., Kuenen J.G., (1989) Aerobic denitrification in various heterotrophic nitrifiers. Antionie van Leeuwenhoek 56, 289-299.

Robertson L.A., Kuenen J.G. (1990). Combined heterotrophic nitrification and aerobic denitrification in *Thiosphaera pantotropha* and other bacteria. *Antonie van Leeuwenhoek.* 57, 139-152.

Robertson L.A., Kuenen J.G. (1992) Nitrogen removal from water and waste microbial control of pollution. Cambridge University Press.

Rohlich G.A. (1948) Measurement and control of sewage treatment process efficiency by oxidation reduction potential. *Sewage Works Journal.* 20(4), 650-653.

Sasaki K., Yamamoto Y., Tsumuara K., Ouchi S., Mori Y. (1996) Development of 2-reactor intermittent-aeration activated sludge process for simultaneous removal of nitrogen and phosphorus. *Wat. Sci. Tech.* 34(1-2), 111.

Sekine T., Iwahorik K., Fujimoto E., Inamori Y. (1985) Advanced control strategies for the activated sludge process: instrumentation and control of water and wastewater treatment and transport systems. *In Proceedings of the 4th IAWPRC Workshop, Houston and Denver. USA.* p.269.

Stensel D.H., Coleman T.E., Denham B.W., Fleischman D. (1995) Innovative process used to upgrade oxidation ditch for nitrogen removal and SVI control. *Presented at the Water Environment Federation 68th annual conference and exposition October 24 1995 Miami Beach Florida.*

Stouthamer A.H., de Boer A.P.N., Van der Oost J. (1997) Emerging principles of inorganic nitrogen metabolism in paracoccus denitrificans and related bacteria. National institute of informacia. Kluwer Academic Publishers 71(1/2), p.33-41.

Strous M., Van Gerben E., Kuenen J.G., Jettern M.S.M. (1997) Effects of aerobic and micro-aerobic conditions on anaerobic ammonium-oxidizing (Anammox). *Applied Environmental Microbiology.* 63, 2446-2448.

Stross M., Van Gerven E., Zheng P., Kuenen J.G. Jetten M.S.M. (1997) Ammonium removal from concentrated waste streams with the anaerobic ammonium oxidation (ANAMMOX) process in different reactor combinations. *Wat. Res.* 31, 1955-1962.

Strous M., Fuerst J. A., Kramer E.H.M., Logemann S., Muyzer G., van de Pas-Schoonen K., Webb R., Kuenen G.J., Jetten M. S. (1999) Missing lithotroph identified as new planctomycete, Nature. 29 July, 400, 446-449.

Strous M. (2000) Microbiology of anaerobic ammonium oxidation. PhD Thesis. Delft University. The Netherlands.

Stumm W. (1966) Redox potential as an environmental parameter: Conceptual significance and operational limitation. *Adv. in Wat. Poll. Res. Proc. of 3rd Int. Conf. of IAWPRC.* Munich Germany. 1, 283-308.

Snoeyink V.L., David J. (1980) Water Chemistry (Text). John Wiley and Son Publishers. ISBN 0-471-05196-9.

Spalding R.F., Exner M.E. (1993) Occurrence of nitrate in groundwater – A review. *Environmental Quality*. 22, 392-402.

Subramaniam K., Keller J., Ho K.M., Johns M.R., Greenfield P.F. (1994) Efficient biological nutrient removal in high strength wastewater using combined anaerobic-sequencing batch reactor treatment. *Wat. Sci. Tech.* 30(6), 319-321.

Subramaniam K., Keller J., Ho K.M., Johns M.R., Greenfield P.F. (1994) Effect of pretreatment on the nutrient removal efficiency in high strength wastewater using SBR technology. *Proceedings of the second Australian conference on biological nutrient removal from wastewater. Albury NSW Australia*. 217-226.

Sutherson S., Ganczarczyk J.J. (1986) Inhibition of nitrite oxidation during nitrification some observations. *Wat. Res.* 21, 257-266.

Suwa Y., Suzuki T., Toyohara H., Yamagishi T., Urushigawa Y. (1992) Single-stage single-sludge nitrogen removal by an activated sludge process with cross-flow filtration. *Wat. Res.* 26(9), 1149-1157.

Tam N.F.Y., Wong Y.S., Leung G. (1992) Significance of external carbon sources on simultaneous removal of nutrients from wastewater. *Wat. Sci. Tech.* 26(5-6), 1047-1055.

Tchobanoglous G., Schroder E.D. (1987) Water Quality (Text) Second Edition. Addison-Wesley Publishing. ISBN 0-201-05433-7.

Thain M., Hickman M. (1996) Dictionary of Biology (Text). Ninth Edition. Penguin Books NZ Ltd 182-190 Wairau Road Auckland 10 New Zealand. ISBN 014-051-288-8.

Thayalakumaran N., Bhamidimarri R., Bickers P.O. (2003) Biological nutrient removal from meat processing wastewater using a sequencing batch reactor. *Wat. Sci. Tech.* 47(10), 101-108.

Third K. (2004) PhD research. University of Murdoch Australia. Supervised by Dr Ralf Cord-Ruwisch senior lecturer in biotechnology, division of science and engineering. South Street Murdoch Western Australia 6150. Email address of Dr Ralf Cord–Ruswisch cord@murdoch.edu.au Tel: (618) 9360 2403.

Tiedje J.M. (1988) Ecology of denitrification and dissimilatory nitrate reduction of ammonium. In biology of anaerobic microorganisms ed A.J.B. Zehnder, pp 179-244. John Wiley and Sons. New York.

Tonkovic Z., Short G., Hansen P. (1997) Nutrient removal experiences at Brushy Creek treatment plant -bulking control and enhanced denitrification. BNR3 conference proceedings. pp297.

Tomlins Z., Thomas M., Keller J., Audic J.M., Urbain V. (2002) Nitrogen removal in a SBR using the OGAR process control system. *Wat. Sci. Tech.* 46(4-5), 125-130.

Turk O., Mavinic D.S. (1986) Preliminary assessment of a shortcut in nitrogen removal from wastewater. *Can. J. Civ. Eng* 13, 600-605.

Turk O., Mavinic D.S. (1987) Selective inhibition: a novel concept for removing nitrogen from highly nitrogenous wastes. *Environmental Technology Letters*. 8, 419-426.

U.S.EPA (1987) Technology transfer design manual phosphorus removal. USEPA/625/1-87/001 CERI Cinn., OH 45268.

Van Niel E.W.J. (1991) Nitrification by heterotrophic denitrifiers and its relationship to autrotrophic nitrification. Ph.D. thesis. Deft University of Technology.

Van Niel E.W.J., Braber K.J., Robertson L.A., Kuenen J.G. (1992) Heterotrophic nitrification and aerobic denitrification in *Alcaligenes faecalis* strain TUD *Antonie van Leeuwenhoek* 62(3), 231-237.

Vanrolleghem P.A., Lee D.S. (2003) On-line monitoring equipment for wastewater treatment processes: state of the art. *Wat. Sci. Tech.* 47(2), 1-34.

Verstraete W. (1975) Heterotrophic nitrification in soil and aqueous media- A Review. *Bull. Acad. Sci, U.S.S.R. Biol. Ser.* 4, 515-530.

Wanner J., Gran P. (1989) Identification of filamentous microorganisms from activated sludge: A compromise between wishes, needs and possibilities. *Wat Res.* 23(7), 883-891.

Wanner J., Kucman K., Ottoua U., Gran P. (1987) Effect of anaerobic conditions on activated sludge in filamentous bulking in laboratory systems. *Wat. Res.* 21(12), 1541-1546.

Wareham D.G., Hall K.J., Mavinic D.S. (1993) Real-Time control of aerobic-anoxic sludge digestion using ORP *Environmental Engineering.* 119(1),120-136.

Wareham D.G., Mavinic D.S., Hall K.J. (1994) Sludge digestion using ORP regulated aerobic anoxic cycles. *Wat. Res.* 28, 373-384.

Watanabe A., Miya A., Matsuo Y. (1984) Laboratory scale study on biological phosphate removal using synthetic wastewater. Newsletter of the IAWPRC study group on phosphate removal. 2, 40-43.

Watanabe S., Baba K., Nogita S. (1985) Basic studies on an ORP/external carbon source control system for the biological denitrification process. Instrumentation and control of water and wastewater treatment and transport systems. *Proceedings 4th IAWPRC Workshop Houston and Denver*, 641-644.

Watanabe Y., Masuda S., Ishiguro M. (1992) Simultaneous nitrification and denitrification in micro-aerobic biofilms. *Wat. Sci. Tech.* 26(3-4), 511-522.

Water and Wastes in NZ (September 1997) page 39. Figure illustrating typical ORP profile, (Original figure slightly modified).

Wentzel M.C., Ekama G.A. (1997) Principle in the design of single sludge systems for biological removal of carbon, nitrogen and phosphorus. *Wat. Res.* 69, 1222-1231.

Westgarth W.C., Sulzer D.A., Okun D.A. (1964) Anaerobiosis in the activated sludge process. Paper presented at the 2nd IAWPRC Conference, Tokyo.

WRC (1984) Theory design and operation of nutrient removal activated sludge processes. *Water Research Commission of South Africa.*

Yang L., Alleman E. (1992) Investigation of a batch wise nitrite build-up by an enriched nitrification culture. *Wat. Sci. Tech.* 26(5-6), 997-1005.

Yoo H., Ahn K.H., Lee H.J., Lee K.H., Kwak Y.J., Song K.G. (1999) Nitrogen removal from synthetic wastewater by simultaneous nitrification and denitrification (SND) via nitrite in an intermittently-aerated reactor. *Wat. Res.* 33(1), 145-154.

Yu R. F., Liaw S.L., Chang C.N., Lu H.J., Chang W.Y. (1997a) The monitoring and control using on-line ORP in the continuous flow activated sludge batch reactor system. *Wat. Sci. Tech.* 35(1),57-66.

Yu R.F., Liaw S.L., Chang C.N., Cheng W.Y. (1998) Applying real-time control to enhance the performance of nitrogen removal in the continuous-flow SBR system. *Wat. Sci. Tech.* 38(3), 271-280.

Zhao W,H., Mavinic D.S., William K.O., Frederic A.K. (1999) Controlling factors for simultaneous nitrification and

denitrification in a two stage intermittent aeration process treating domestic sewage. *Wat. Res.* 33(4), 961-970.

Zheng H., Hanaki K., Matsuo T. (1995) Production of nitrous oxide gas during nitrification of wastewater. *Wat. Sci. Tech.* *, (*), 103-111. *Information unavailable.

Zipper T., Fleischmann N., Hanerl R. (1998) Development of a system for control and optimization of small wastewater treatment plants using oxidation-reduction potential (ORP). *Wat. Sci. Tech.* 38(3), 307-314.